m.p. 154–157°, was obtained in 76.3% yield. After recrystallization from ethyl alcohol it meltedat 163–164°. A mixed melting point with product obtained from method V or VI gave no depression.

Anal. Calcd. for $C_9H_{10}N_2O_3$: N, 14.42; H, 5.19; C, 55.66. Found: N, 14.50; H, 5.16; C, 55.86.

3-(*p*-Nitrosoanilino)-propionitrile (XLVII).—The same procedure described for the preparation of β-(*p*-nitrosoanilino)-propionic acid (method V) was employed except 43.8 g. (0.25 mole) of 3-(N-nitrosoanilino)-propionitrile XVIII was replaced for the β-(N-nitrosoanilino)-propionic acid. The product, a green colored solid, m.p. 127–129°, was obtained in 67.5% yield. After recrystallization from ethyl alcohol it melted at 132–133°.

Anal. Calcd. for $C_9H_9N_3O$: H, 5.18; C, 61.70; N, 23.99; mol. wt., 175.2. Found: H, 4.97; C, 61.85; N, 23.91; mol. wt., 172.7.

Methyl β-(2,4-Dinitroanilino)-propionate (XLVIII).—To a stirred solution of 30 ml. of concd. nitric acid and 90 ml. of water, 40 g. (0.19 mole) of methyl (*p*-nitrosoanilino)-propionate (XLIII) was added in ten portions at 40–50° over a 15-minute period. The stirred reaction mixture was maintained at 40–50° for an additional 20 minutes, poured into 1,000 g. of ice-water and neutralized with concd. ammonium hydroxide until a *p*H 8 was obtained. The solid was collected by filtration, washed with water until the washings were neutral to litmus and air-dried at 25–30°. The product, a light brown solid, m.p. 69–70°, was obtained in 79.2% yield. After recrystallization from ethanol it melted at 72–73°.

Anal. Calcd. for $C_{10}H_{11}N_3O_6$: N, 15.61. Found: N, 15.98.

N,4-Dinitroso N-Substituted Anilines (XLIX-LV).—To a stirred slurry containing 0.2 mole of the appropriate N-substituted *p*-nitrosoaniline and 1000 g. of ice-water, 24 ml. of concd. hydrochloric acid was added in one portion. To this stirred solution at 0° was added dropwise at 0–10°, 14.4 g. (0.203 mole) of 97% sodium nitrite dissolved in 30 ml. of water over a 30-minute period. To the resulting slurry 200 ml. of heptane was added and stirring was continued for one hour at 10–20°. The solid was collected, washed successively with 500 ml. of cold water and heptane and air-dried at 25–30°. The data are summarized in Table IV.

Dicyclohexylamine Salt of β-(*p*-Nitrosoanilino)-propionic Acid (LVI).—To a stirred slurry containing 19.4 g. (0.1 mole) of β-(*p*-nitrosoanilino)-propionic acid (XLVI) in 200 ml. of dry benzene was added in one portion 36.3 g. (0.2 mole) of dicyclohexylamine. After stirring for four hours at 25–30°, the solid was collected, washed with 200 ml. of ethyl ether and air-dried at 25–30°. The product, a green colored solid, m.p. 162–167° with decomposition, was obtained in 99% yield.

Anal. Calcd. for $C_{21}H_{33}N_3O_3$: N, 11.19. Found: N, 10.95.

***p*-Nitrosophenyl Substituted Ureas (LVII–LVIX).**—To 0.2 mole of β-(*p*-nitrosoanilino)-propionic acid (XLVI) or methyl β-(*p*-nitrosoanilino)-propionate (XLIII) in 300 ml. of heptane was added in one portion 0.22 mole of toluene 2,4-diisocyanate or 4,4′-methylenediphenol isocyanate. The stirred reaction mixture was maintained at 25–30° for 24 hours. The product was collected by filtration and air-dried at 25–30°. The data are summarized in Table V.

Metal Salts of N-Substituted *p*-Nitrosoanilines (LX-LXIV).—To a stirred slurry containing 0.2 mole of the appropriate N-substituted *p*-nitrosoaniline, 32 g. (0.2 mole) of 25% aqueous sodium hydroxide and 1000 ml. of water was added in one portion a solution containing 0.1 mole of either nickel nitrate hexahydrate, zinc chloride, copper sulfate pentahydrate or cadmium sulfate ($3\ CdSO_4.8H_2O$) in 500 ml. of water. The reaction mixture was stirred for one hour at 25–30°. The solid was collected, washed with water until the washings were neutral to litmus and air-dried at 25–30°. The data are summarized in Table VI.

Copper Salt of β-(*p*-Nitrosoanilino)-propionic Acid (LXV).—To a stirred solution containing 19.4 g (0.1 mole) of β-(*p*-nitrosoanilino)-propionic acid (XLVI), 16 g. (0.1 mole) of 25% aqueous sodium hydroxide and 500 ml. of water was added in one portion 12.5 g. (0.05 mole) of copper sulfate pentahydrate dissolved in 500 ml. of water. After stirring for one hour at 25–30°, the solid was collected by filtration, washed with water until the washings were neutral to litmus and air-dried at 25–30°. The product, a green colored solid, was obtained in 49.7% yield.

Anal. Calcd. for $C_{18}H_{18}N_4O_6Cu{\cdot}4H_2O$: Cu, 12.17. Found: Cu, 11.60.

β-(2,4-Dihydroxy-3,5-dinitrosophenyl)-propionic Acid Hydrate.—To a stirred suspension at 0° containing 45.6 g. (0.25 mole) of β-(2,4-dihydroxyphenyl)-propionic acid, 29 g. of concd. hydrochloride acid, 150 ml. of ethyl alcohol and 500 ml. of water was added dropwise at 0–10° a solution containing 40 g. (0.56 mole) of 97% sodium nitrite in 100 ml. of water. After stirring for an additional hour at 0–10° the solid was collected, washed with cold water until free of chloride and air-dried at 25–30°. The product, m.p. 110–115° with decomposition, was obtained in 46.6% yield. After recrystallization from water it melted at 128–130° with decomposition.

Anal. Calcd. for $C_9H_8N_2O_6{\cdot}H_2O$: N, 10.53. Found: N, 10.67.

Acknowledgment.—The writers wish to acknowledge their indebtedness to Messrs. R. O. Zerbe, T. W. Bartram and D. Mullins for assistance during the course of this investigation. Grateful acknowledgment also is made for the analyses by Mr. E. E. Null.

NITRO, W. VA.

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

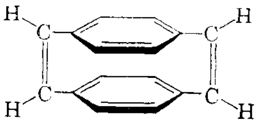
Macro Rings. XIX. Olefinic Paracyclophanes[1]

BY DONALD J. CRAM AND KENNETH C. DEWHIRST

RECEIVED FEBRUARY 14, 1959

A number of classically-conjugated olefinic paracyclophanes have been prepared based on the ring systems of [4.4]paracyclophane and of [2.2.2]paracyclophane. The peculiar geometry and symmetry properties of [4.4]paracyclophane which contains four double bonds is discussed. The spectral properties of these compounds are reported and correlated with their configurations.

An earlier paper[2] reported the preparation of unsaturated derivatives of [2.2]paracyclophane such as I, which serve as extreme examples of steric inhibition of resonance. This paper reports the preparation and properties of a number of paracyclophanes which contain double bonds in the bridges connecting the aromatic nuclei. These compounds are all based on the [2.2.2]paracyclophane (II) or



I

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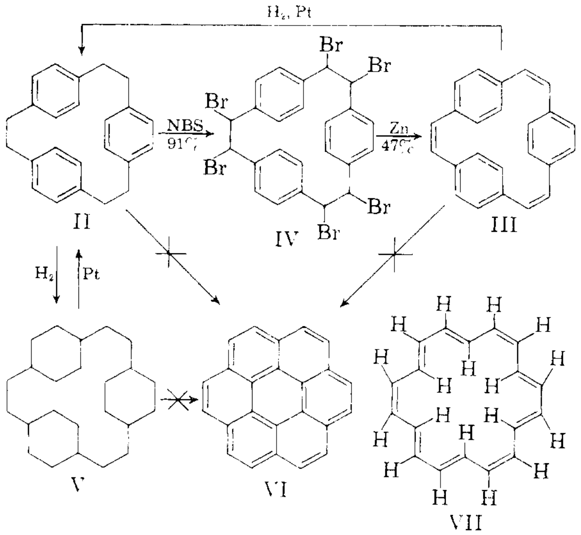
[1] This work was supported in part by a grant from the Upjohn Co.

[2] K. C. Dewhirst and D. J. Cram, THIS JOURNAL, **80**, 3115 (1958).

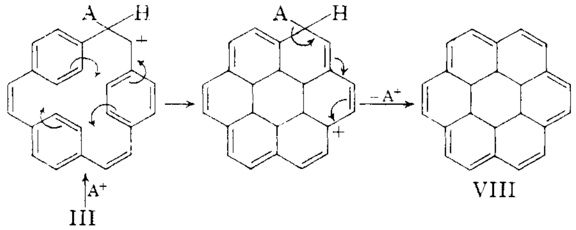
[4.4]paracyclophane ring systems, which are more flexible than the ring system of I, but which still prevent the atoms bound by unsaturated linkages from occupying the same plane.

Preparation of Triene of [2.2.2]Paracyclophane.—Triene III was prepared from paracyclophane II[3] with hexabromide IV as an intermediate. Catalytic reduction of II gave the fully saturated cycle V, which upon dehydrogenation gave back paracyclophane II. No coronene (VI) was produced during the dehydrogenation, nor could this fully aromatic compound be produced from either II or III by treatment with Lewis acids or dehydrogenating agents.



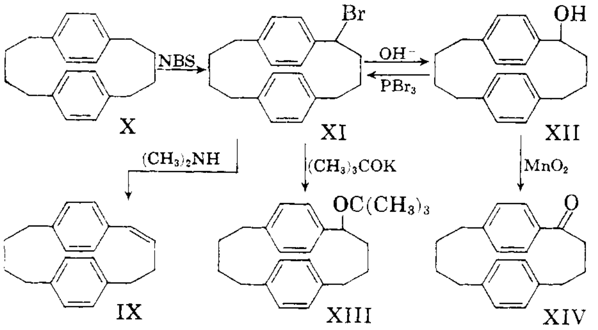
Triene III is of interest because of its relationship to compound VII, which should be planar, which contains 18 π-electrons, and which should be a non-benzenoid aromatic. Although triene III contains the same peripheral electronic system, the three benzene rings cannot occupy the same plane for steric reasons. Molecular models suggest that two of the three benzene rings of III can become somewhere near coplanar, but that the plane of the third then becomes almost perpendicular to the plane of the first two.

Compounds III and VIII are valence tautomers of one another. Molecular models of VIII suggest the peripheral system of double bonds in the molecule should be close enough to being coplanar for the system to possess aromatic character. Attempts were made to convert triene III into polyene VIII with acids and with light as catalysts. Although a reaction path of the type indicated is probably available to the system, the reaction did not occur. Probably the resonance energy of the three benzene rings of III is greater than that of VIII, and the equilibrium mixture, if established, favors III.

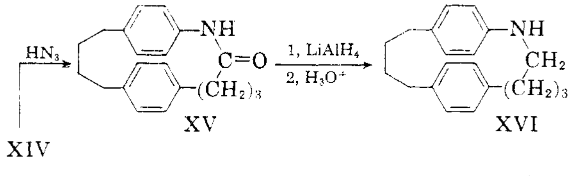


Preparation of Olefins Derived from [4.4]Paracyclophane.—The conjugated monoölefin IX was prepared from the parent [4.4]paracyclophane (X) by the method outlined in Chart I. Bromide XI hydrolyzed while adsorbed on a column of basic alumina to give alcohol XII. When treated with boron trifluoride-etherate, a high-melting hydrocarbon was produced which analyzed for olefin IX, but whose infrared and ultraviolet spectra gave no indication of a carbon–carbon double bond. This substance might be a dimer of IX. Bromide XI gave substitution product XIII when mixed with potassium *t*-butoxide, and olefin IX when heated with dimethylamine at 110°. This olefin is an unstable solid which reacts rapidly with oxygen of the air. Its infrared spectrum suggests that the sample is a mixture of *cis* and *trans* isomers, molecular models of which appear equally probable.

CHART I



Ketone XIV (prepared from XII) when treated with hydrazoic acid gave amide XV which was reduced to amine XVI. That phenyl and not methylene migrated in the rearrangement was demonstrated by the fact that amine XVI possesses an ultraviolet absorption spectrum characteristic of an aniline derivative. The spectrum is changed in acid solution (see Fig. 1).



Diene XVII was synthesized as shown in Chart II. Acyloin XVIII[4] was reduced to diol XIX which when dehydrogenated with palladium gave open-chain compound XX. Similar cleavages have been observed[5] during dehydrogenation of tetralin derivatives, but could be avoided by use of acetylated derivatives.[5] When bis-acetate XXII was treated with palladium, [4.4]paracyclophane (X) was produced in 78% yield. This transformation probably involved an elimination reaction fol-

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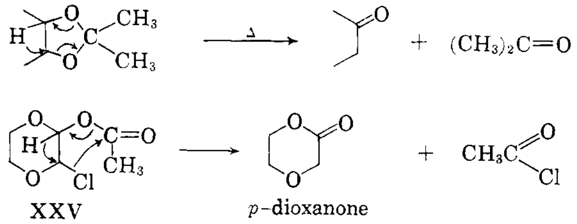
(3) W. Baker, J. F. W. McOmie and J. M. Norman, *J. Chem. Soc.*, 1114 (1951).

(4) D. J. Cram and N. L. Allinger, THIS JOURNAL, **76**, 726 (1954).

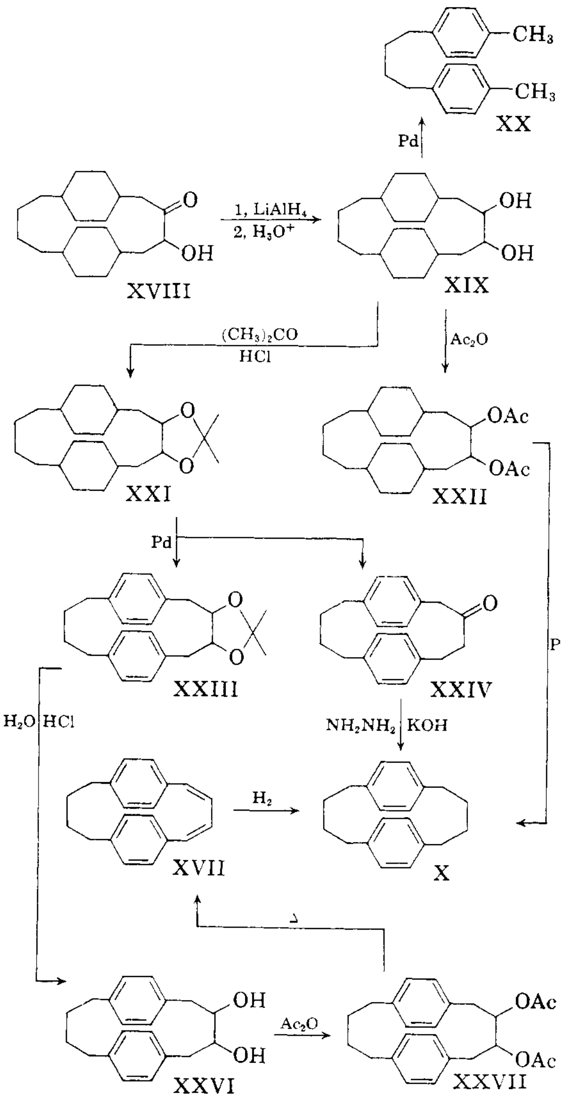
(5) M. S. Newman and H. V. Zahm, *ibid.*, **65**, 1097 (1943).

lowed by hydrogen-disproportionation on the surface of the catalyst.[6] Acetonyl derivative XXI of the diol when treated with palladium gave a 38% yield of the desired aromatic derivative XXIII, and ketone XXIV, which must have involved hydrogen migration during the reaction. This latter reaction may be general, and probably follows a general mechanism of the type indicated.



XXV p-dioxanone

CHART II



An analogous reaction is found in the pyrolytic formation of p-dioxanone from 1-acetoxy-2-chloro-p-dioxane (XXV).[7]

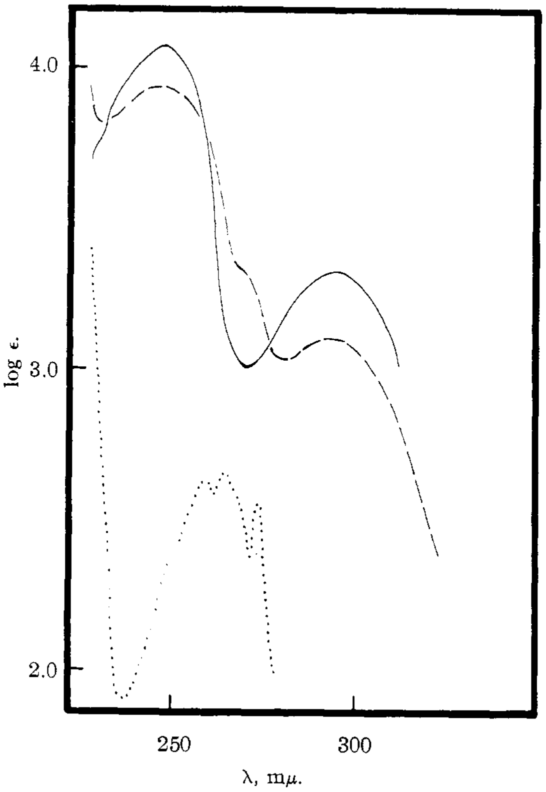
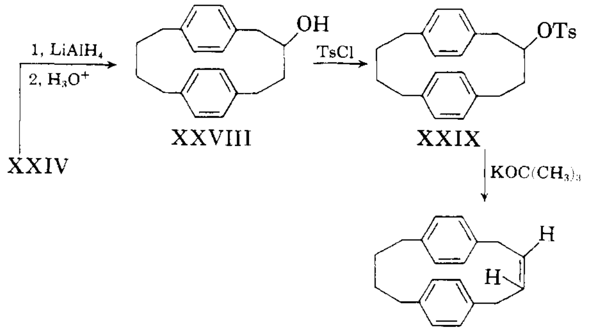


Fig. 1.—Ultraviolet absorption spectra: curve – – – –, amine XVI in 95% ethanol; curve . . . . . ., amine XVI in 95% ethanol 0.01 molar in hydrogen chloride; curve ———, N-methylaniline model.

Acetononide XXIII was hydrolyzed to diol XXVI, whose acetyl derivative XXVII gave diene XVII when pyrolyzed. This substance when catalytically reduced gave [4.4]paracyclophane (X). A maleic anhydride adduct of diene XVII could not be prepared. Molecular models of the substance suggest that both double bonds are *cis*, and support for such a structure is found in the similarity between the ultraviolet spectrum of XVII and that of *cis,cis*-1,4-diphenylbutadiene (see Fig. 2).

Ketone XXIV (Chart I) was converted to the unconjugated olefin XXX by the steps indicated. The final elimination reaction with potassium *t*-butoxide went in 55% yield, and unexpectedly gave unconjugated *trans*-olefin. The structure of this compound was demonstrated by the lack of strong absorption in the 245 mμ region of the ultraviolet,



XXX

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(6) E. H. Braude, R. P. Linstead and P. W. D. Mitchell, *J. Chem. Soc.*, 3578 (1954).

(7) R. K. Summerbell and H. W. Lunk, THIS JOURNAL, **80**, 604 (1958).

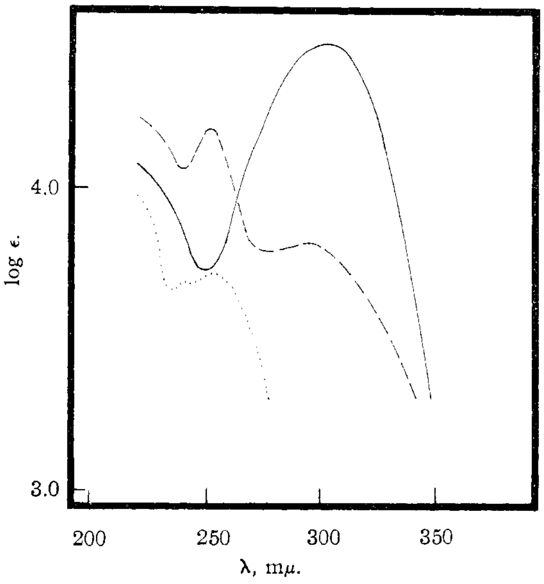
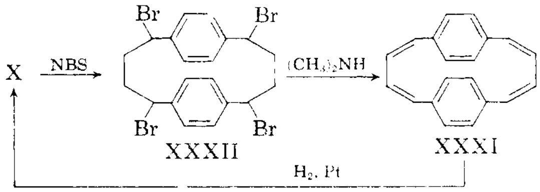


Fig. 2.—Ultraviolet absorption spectra in 95% ethanol: curve – – – –, 1,4-diphenylbutadiene; curve ———, diene XVII; curve ……, monoene IX.

and by the presence of a strong band at 953 cm.$^{-1}$ in the infrared which is characteristic of a *trans*-olefin. When catalytically reduced, olefin XXX gave [4.4]paracyclophane (X).

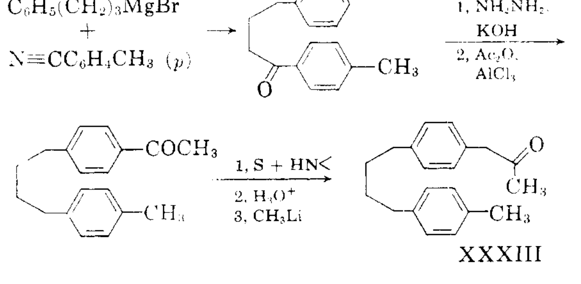
Two factors probably contribute to the production of unconjugated *trans*-olefin rather than the expected conjugated olefin in the above elimination reaction. The benzyl hydrogen is more hindered than the other hydrogen, and some of the electronic advantage to formation of conjugated olefin is lost due to steric inhibition of resonance in this cyclic system.

Tetraolefin XXXI was prepared with [4.4]paracyclophane as the starting material. Treatment of this cycle with N-bromosuccinimide gave a mixture of tri- and tetrabromides. The latter compound (XXXII) when heated to 140° with dimethylamine gave a 4% yield of the completely conjugated olefin XXXI, which upon catalytic reduction gave back [4.4]paracyclophane (X).



XXXII XXXI

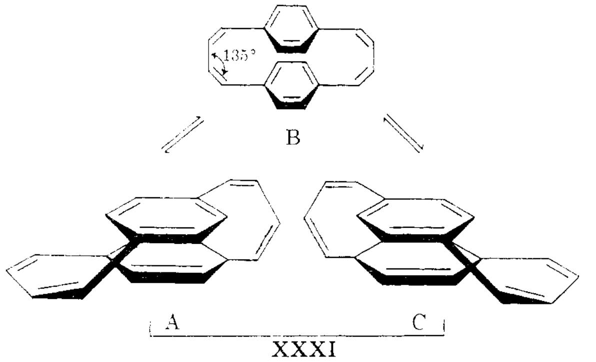
Compound XXXIII was desired as a model for ketone XXIV in spectral studies (see next section), and was synthesized by the reaction scheme indicated.



XXXIII

Discussion

Symmetry Properties of Tetraolefin XXXI.—In structure B for olefin XXXI, the eight carbons of the bridges are written in a plane which is perpendicular to the planes occupied by the two benzene rings. Although this structure is analogous to that for I, the eight carbon–carbon–carbon bond angles of the two bridges are equal to 135° rather than 120°, which is normal for such linkages. This strain is relieved by rotation of the top benzene ring 60° about an axis which passes through the center of both benzene rings. Counterclockwise rotation gives conformation A, and clockwise rotation gives C. Thus B possesses a configuration of higher energy than A and C, and serves as a model for the transition state which intervenes between conformations A and C, which are of equal energy. Conformations A and C contain neither planes nor centers of symmetry and are mirror images and non-superimposable on one another. The question of whether the activation energy for interconverting A and C is great enough to allow resolution of XXXI into optically active antipodes is currently being examined.



XXXI

Steric Modifications of Spectral Properties.—In contrast to the [2.2]paracyclophane system, introduction of unsaturated functions into the [4.4]paracyclophane system causes large spectral exaltations. Nevertheless, the system imposes enough restriction on the configuration of various chromophores to cause marked spectral shifts compared with the corresponding open-chain compounds.

The band in the ultraviolet spectrum of diolefin XVII (Fig. 2) which occurs at longer wave length is found at shorter wave length and lower intensity than that of its structural analog, *cis,cis*-1,4-diphenylbutadiene (Fig. 2). In contrast, the short wave length band of XVII shows a marked shift to longer wave length and higher intensity. This band occurs at about the same wave length as that of monolefin IX (Fig. 2). The movements of both bands of XVII may be plausibly ascribed to an increased probability of "half chromophore" resonance[8] due to distortion of the whole system from planarity. The short wave length bands of *cis*- and *trans*-stilbene exhibit a similar behavior.[9]

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[8] L. Zechmeister, *Chem. Revs.*, **34**, 267 (1944).

[9] R. N. Beale and E. M. F. Roe, *J. Chem. Soc.*, 2755 (1953).

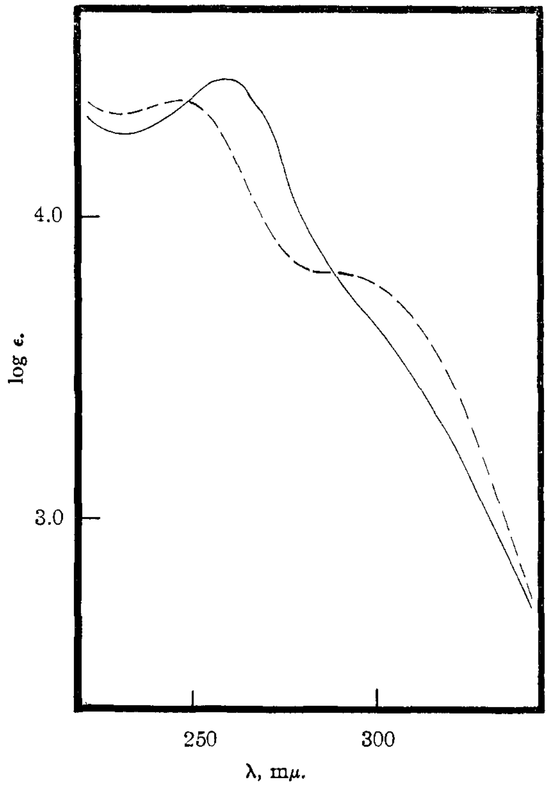

Fig. 3.—Ultraviolet absorption spectra in 95% ethanol: curve – – – –, tetraene XXXI; curve ———, triene III.

Figure 3 records the ultraviolet spectra of triene III and tetraene XXXI. Effects similar to those observed for diene XVII are visible in these spectra. The two curves are rather similar, and have been shifted to considerably shorter wave lengths compared with any reasonable open-chain model. For example, 1,8-diphenyloctatetraene absorbs at 410 mμ.[10] As expected, the long wave length band of tetraene XXXI occurs at shorter wave lengths and lower intensities than that of triene III, since the former presents larger steric barriers to planarity of its chromophores than III. The same effect is reflected by the shift to longer wave lengths and higher intensities of the "half chromophore" band, which in the tetraene is almost identical to that of *p*-divinylbenzene (261 mμ).[11]

Other effects are visible in the spectra of Fig. 4. The position of the main absorption band of these conjugated aromatic ketones remains essentially constant, while the extinction coefficient decreases regularly in passing from the open-chain model to 1-keto[6.6]paracyclophane[12] to 1-keto[4.4]paracyclophane (XIV). This behavior is consistent with that of other aromatic ketones in which the populations of the planar or near-planar forms are decreased for steric reasons.[13] Calculation of the interplanar angle (θ) between the carbonyl and phenyl groups from the relationship, $\cos^2 \theta = \epsilon_0/\epsilon$ (ϵ_0 is the molar extinction coefficient of the model compound),[13] gives values of 24° and 42° for 1-keto[6.6]paracyclophane and 1-keto[4.4]paracyclophane, respectively. These values are consistent with expectations derived from an inspection of molecular models of the substances.

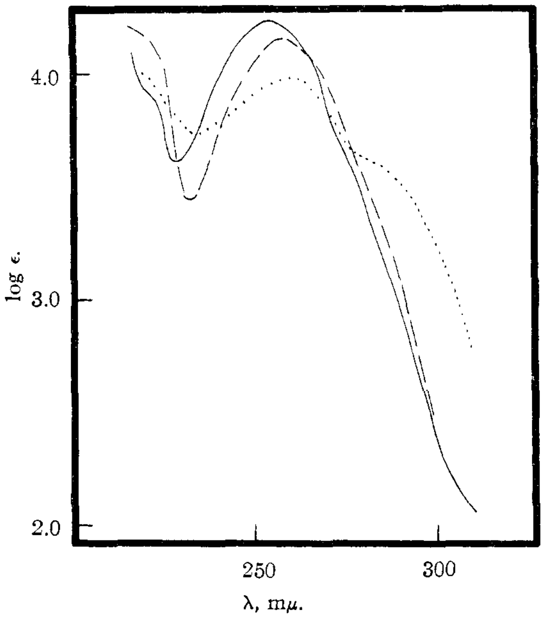

Fig. 4.—Ultraviolet absorption spectra in 95% ethanol: curve ———, 1-(4-methylphenyl)-4-(4-acetylphenyl)-butane; curve – – – –, 1-keto[6.6]paracyclophane; curve . . . . . ., 1-keto[4.4]paracyclophane.

The spectra of a number of unconjugated ketones are recorded in Fig. 5. The differences in the spectra of the saturated ketone on the one hand and ketones XXIV and XXXIII on the other illustrate the well known fact that the absorption band associated with the N → A transition of an isolated carbonyl group moves to longer wave lengths and higher intensities by the introduction of an α-phenyl group.[14] Fusion of the α-phenylcarbonyl structural unit into a ring as in ketone XXIV results in a further shift of this band to longer wave length and higher intensity as compared to the open-chain model XXXIII. This additional effect must be associated with the restriction of internal rotations in cycle XXIV which holds the phenyl and carbonyl chromophores in a more favorable geometry for interaction than is found in the more freely-rotating open-chain model. Molecular models suggest that the planes of the phenyl and of the carbonyl groups tend to be perpendicular to one another in cycle XXIV, and that the *p*-orbitals of these functions are pointed toward one another along axes approximately perpendicular to one another. Others[14b] have come to similar conclusions with respect to the best geometry for enhanced absorption in β,γ-unsaturated ketones.

Experimental

Boiling points and melting points are corrected. Ultraviolet absorption spectra were all taken in 95% ethanol, Cary recording spectrometer, model 11 MPS.

1-Hydroxy[4.4]paracyclophane (XII).—A mixture of 1.0 g. of [4.4]paracyclophane (X),[4] 0.52 g. of N-bromosuccini-

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[10] K. W. Hausser, R. Kuhn and G. Z. Seitz, *Z. physik. Chem.*, **B29**, 391 (1935).

[11] S. D. Ross and M. Markarian, *J. Polymer Sci.*, **9**, 222 (1952).

[12] D. J. Cram and R. A. Reeves, THIS JOURNAL, **80**, 3094 (1958).

[13] E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, 3754 (1955).

[14] (a) W. D. Kumler, L. A. Strait and E. L. Alpen, THIS JOURNAL, **72**, 1463 (1950); (b) R. C. Cookson and N. S. Wariyar, *J. Chem. Soc.*, 2302 (1956); (c) R. C. Cookson and N. Lewin, *Chemistry & Industry*, **37**, 984 (1956).

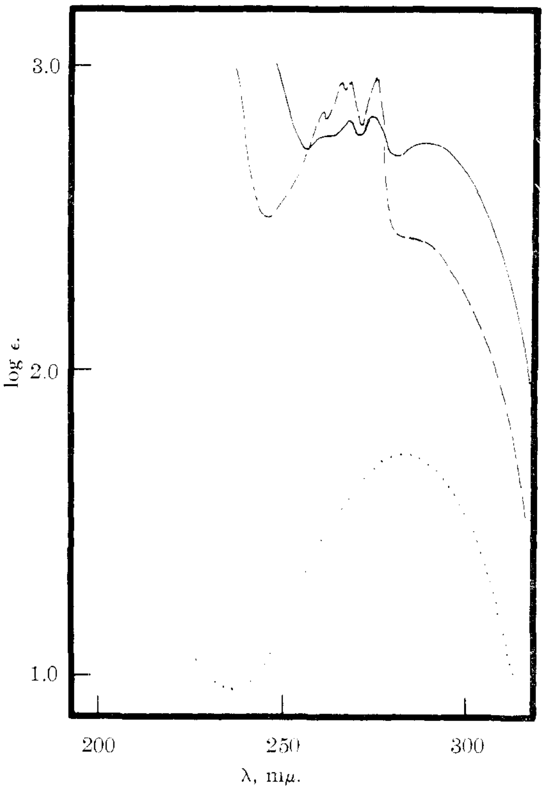

Fig. 5.—Ultraviolet absorption spectra in 95% ethanol: curve ———, unconjugated ketone XXIV; curve – – – –, open-chain ketone XXXIII; curve ......, 2-keto-5,6,7,8,9,10,15,16,17,18,19,20-dodecahydro[4.4]paracyclophane.

mide and 50 ml. of carbon tetrachloride was refluxed for 3 hours. The mixture was filtered to remove succinimide, and the resulting solution was washed with sodium bicarbonate solution and with water. The carbon tetrachloride layer was evaporated, and the residue was adsorbed on a column of basic alumina of activity I.[15] Elution of the column with pentane gave 0.42 g. (42%) of starting material and elution with ether gave 0.305 g. (29%) of product, m.p. 150–153°. More highly hydroxylated material (100 mg.), m.p. 160–200°, was obtained upon elution of the column with methanol. For analysis, a small sample of the monohydroxy compound XII was recrystallized 3 times from benzene–hexane, m.p. 154.6–155.6°.

Anal. Calcd. for $C_{20}H_{24}O$: C, 85.67; 8.63. Found: C, 85.54; H, 8.41.

1-Keto[4.4]paracyclophane (XIV).—Alcohol XII, 580 mg., was shaken with 6 g. of manganese dioxide in 100 ml. of chloroform at 40° for 4 days. The mixture was filtered to remove maguesese dioxide, concentrated, and adsorbed on a column of neutral alumina of activity I.[15] Elution of the column with 40% ether–pentane gave 390 mg. (67%) of product, m.p. 111–113°. This material was undepressed upon admixture with an authentic sample,[12] m.p. 113–114°. Elution of the column with ether gave 120 mg. (21%) of starting material.

1-Aza-2-keto[4.5]paracyclophane (XV).—Monoketone XIV, 145 mg., 1.5 g. of trichloroacetic acid and 100 mg. of sulfuric acid were mixed and heated to 60°. Sodium azide, 50 mg., was then added in one portion, and the solution was maintained at 60° for 10 minutes. The solution was then cooled, diluted with water, neutralized with ammonium hydroxide, and extracted with ether. The ether extract was washed with water, dried, and evaporated to give 140 mg. of crude material, m.p. 190–198°. One crystallization of this material from ethanol–water gave 104 mg. (67%) of pure product XV, m.p. 202–204°. For analysis, a small sample was recrystallized 4 times from ethanol–water, m.p. 204.0–206.4°.

Anal. Calcd. for $C_{20}H_{23}ON$: C, 81.87; H, 7.90. Found: C, 81.63; H, 8.13.

1-Aza[4.5]paracyclophane (XVI).—Amide XV, 240 mg., 300 mg. of lithium aluminum hydride and 200 ml. of ether were placed in a Soxhlet extractor and refluxed for 24 hours. The mixture was cooled in an ice-bath, treated with a small amount of water, and shaken with 50 ml. of 20% sodium potassium tartrate solution. The ether layer was separated and extracted with 2 *N* hydrochloric acid. The hydrochloric acid layer was cooled, neutralized with sodium hydroxide, and extracted with ether. The ether layer was separated, washed with water, dried and evaporated to give 125 mg. (52%) of product, m.p. 143–145°. For analysis, a small sample was recrystallized 4 times from ethanol–water, m.p. 146.0–146.8°.

Anal. Calcd. for $C_{20}H_{25}N$: C, 85.97; H, 9.02. Found: C, 85.75; H, 8.85.

Treatment of 1-Hydroxy[4.4]paracyclophane (XII) with Boron Trifluoride.—Alcohol XII, 90 mg., was dissolved in a mixture of 2 ml. of glacial acetic acid and 1 ml. of boron trifluoride–etherate, and the resulting solution was allowed to stand at room temperature for 3 hours. The reaction mixture was diluted with water, extracted with ether, and the ether layer was evaporated. The residue was chromatographed on neutral alumina, and the eluate was evaporated and crystallized from benzene–hexane to give 25 mg. (30%) of hydrocarbon, m.p. 227–230°. For analysis, a small sample was twice recrystallized from benzene–hexane, m.p. 228.0–230.0°.

Anal. Calcd. for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.70; H, 8.62.

The compound did not react with potassium permanganate, and exhibited only benzenoid absorption in the ultraviolet and infrared. These facts, coupled with the high melting point of the compound, suggest that dimerization has occurred.

1-Bromo[4.4]paracyclophane (XI).—Alcohol XII, 280 mg., 0.032 ml. of phosphorus tribromide and 5 ml. of ether were mixed, refluxed for 5 hours, and allowed to stand overnight at room temperature. The reaction mixture was then washed with water, dried and evaporated to give 343 mg. (100%) of product, m.p. 110–115°. This material was crystallized once from benzene–hexane, m.p. 113–114°. In order to conserve material, an analytical sample was not prepared. The bromide was used directly in the next experiments.

1-*t*-Butoxy[4.4]paracyclophane (XIII).—Bromide XI, 170 mg., was refluxed under nitrogen with 2 ml. of 1 *M* potassium *t*-butoxide in *t*-butyl alcohol for 1 hour. The reaction mixture was cooled, diluted with water, and extracted with ether. The ether layer was evaporated and the residue was chromatographed on alumina and crystallized from ethanol–water to give 35 mg. (21%) of product, m.p. 100–103°. For analysis, a small sample was recrystallized 4 times from ethanol–water, m.p. 108.2–108.6°.

Anal. Calcd. for $C_{24}H_{32}O$: C, 85.66; H, 9.59. Found: C, 85.74; H, 10.05.

1,2-Dehydro[4.4]paracyclophane (IX).—Bromide XI, 170 mg., was heated with dimethylamine (containing a little benzene) in a sealed tube at 110° for 24 hours. The reaction mixture was cooled, stripped of dimethylamine, diluted with ether, and washed with dilute potassium hydroxide. The ether layer was evaporated, and the residue was adsorbed on a column of neutral alumina of activity I.[15] Elution of the column with pentane gave 33 mg. (25%) of product, m.p. 68–71°. For analysis, a small sample was recrystallized 4 times from methanol–water, m.p. 75.8–77.5°.

Anal. Calcd. for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 90.91; H, 8.22.

The material reacts rapidly with potassium permanganate and with oxygen in the air. After exposure to the air for two days; IX gave a carbonyl band at 1700 cm.$^{-1}$ in the infrared.

2,3-Dihydroxyperhydro[4.4]paracyclophane (XIX).—Acyloin XVIII,[4] 613 mg. in 50 ml. of ether, was added slowly to a stirred slurry of 170 mg. of lithium aluminum hydride in 100 ml. of ether, and the resulting mixture was refluxed for 1 hour. The mixture was cooled in an ice-bath and cautiously decomposed consecutively with ethyl acetate and dilute hydrochloric acid. The ether layer was separated and washed successively with dilute hydrochloric acid, sodium bicar-

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[15] H. Brockmann and H. Schodder, *Ber.*, **74B**, 73 (1941).

bonate solution, and water. Evaporation of the ether layer and crystallization of the residue from benzene–hexane gave 591 mg. (96%) of product, m.p. 176–179°. For analysis, a small sample was recrystallized 4 times from benzene–hexane, m.p. 176.8–179.0°.

Anal. Calcd. for $C_{20}H_{36}O_2$: C, 77.86; H, 11.44. Found: C, 77.97; H, 11.55.

In a larger run, one pure diastereomer, m.p. 181.0–182.0°, could be isolated in 85% yield. This material showed no carbonyl band in the infrared, and was depressed upon admixture with a sample of XVIII.

Treatment of 2,3-Dihydroxyperhydro[4.4]paracyclophane (XIX) with Palladium-Carbon.—Diol XIX, 1.5 g., was mixed with 150 mg. of palladium–carbon and heated at 300° for 2 hours. During this time, 140% of the theoretical amount of 6 molar equivalents of hydrogen was evolved. The reaction mixture was cooled, diluted with pentane, and filtered to remove the palladium–carbon. The filtrate was evaporated, and the residue was crystallized from ethanol–water to give 630 mg. (56%) of 1,4-bis-(*p*-tolyl)-butane (XX), m.p. 69–72°. Two recrystallizations of this material raised the melting point to 74.4–75.2°, undepressed upon admixture with an authentic sample of XX.[16]

2,3-Diacetoxyperhydro[4.4]paracyclophane (XXII).—Diol XIX, 1.0 g., 4.0 g. of acetic anhydride and 10 ml. of dry pyridine were mixed and refluxed for 5 minutes. The reaction mixture was cooled, diluted with water, and extracted with chloroform. The chloroform layer was successively washed with dilute hydrochloric acid, sodium bicarbonate solution and water. Evaporation of the chloroform layer gave 1.2 g. (94%) of product, a colorless oil. For analysis, a small sample was chromatographed and distilled to give a clear glass.

Anal. Calcd. for $C_{24}H_{40}O_4$: C, 73.43; H, 10.27. Found: C, 73.45; H, 10.38.

Treatment of 2,3-Diacetoxyperhydro[4.4]paracyclophane (XXII) with Palladium-Carbon.—Diacetate XXII, 1.2 g., was mixed with 120 mg. of palladium–carbon and heated slowly to a maximum temperature of 320°. Acetic acid distilled from the reaction mixture, and hydrogen evolution stopped at 67% of the theoretical value of 6 mole equivalents. The reaction mixture was cooled, diluted with pentane, and filtered to remove the palladium–carbon. Evaporation of the filtrate gave 630 mg. (78%) of [4.4]paracyclophane (X), m.p. 145–147°. One crystallization of this material from ethanol raised the melting point to 146.4–147.2°, undepressed upon admixture with an authentic sample of X.

2,3-Dihydroxyperhydro[4.4]paracyclophane Acetonide (XXI).—Diol XIX, 5.0 g., 250 ml. of dry acetone (pretreated with hydrogen chloride gas to *p*H 1), and a small quantity of anhydrous sodium sulfate were mixed and stirred at room temperature for 28 hours. The mixture was then neutralized with ammonia gas and filtered to remove inorganic salts. Evaporation of the filtrate gave 5.25 g. (93%) of product, m.p. 126–128°. For analysis, a small sample was crystallized from acetone, m.p. 126.0–127.8°.

Anal. Calcd. for $C_{23}H_{40}O_2$: C, 79.25; H, 11.57. Found: C, 79.09; H, 11.35.

Treatment of 2,3-Dihydroxyperhydro[4.4]paracyclophane Acetonide (XXI) with Palladium-Carbon.—Acetonide XXI, 7.85 g., was mixed with 800 mg. of palladium–carbon and heated at 300° for 4.5 hours. The reaction mixture was cooled, diluted with benzene, and filtered to remove the palladium–carbon. The filtrate was concentrated and adsorbed on a column of neutral alumina of activity *ca.* IV.[15] The column was eluted with pentane, and a total of 75 200-ml. fractions were collected: fractions 1–10 gave 1.2 g. of a mixture of hydrocarbons; fractions 11–50 gave 2.90 g. (38%) of 2,3-dihydroxy[4.4]paracyclophane acetonide (XXIII), m.p. 162–163°; and fractions 51–75 gave 1.55 g. (25%) of 2-keto[4.4]paracyclophane (XXIV), m.p. 153–154°. For analysis, a small sample of acetonide XXIII was crystallized from acetone, m.p. 162.8–163.5°.

Anal. Calcd. for $C_{23}H_{28}O_2$: C, 82.10; H, 8.39. Found: C, 81.90; H, 8.37.

For analysis, a small sample of ketone XXIV was crystallized from benzene–hexane, m.p. 154.4–155.4°.

Anal. Calcd. for $C_{20}H_{22}O$: C, 86.28; H, 7.97. Found: C, 86.33; H, 8.24.

A 2,4-dinitrophenylhydrazone of XXIV was prepared in the usual manner, m.p. 235–237°.

Anal. Calcd. for $C_{26}H_{26}O_4N_4$: C, 68.10; H, 5.72. Found: C, 68.07; H, 5.80.

Wolff-Kishner Reduction of 2-Keto[4.4]paracyclophane (XXIV).—Ketone XXIV, 50 mg., was added to a solution of hydrazine and potassium hydroxide in diethylene glycol, and the resulting solution was refluxed for 1.5 hours. At the end of this time, the reflux condenser was removed until the boiling solution reached a temperature of 200°. The condenser was then replaced, and the solution was allowed to reflux overnight. The reaction mixture was cooled, diluted with water, and extracted with ether. The ether layer was dried and evaporated to give 36 mg. (76%) of [4.4]paracyclophane(X), m.p. 143–145°. Crystallization of this material from ethanol raised the melting point to 146.6–147.4°, undepressed upon admixture with an authentic sample of X.

2-Hydroxy[4.4]paracyclophane (XXVIII).—Ketone XXIV, 580 mg., was slowly added in 50 ml. of ether to a slurry of 152 mg. of lithium aluminum hydride in 50 ml. of ether. The mixture was refluxed for an hour, cooled, and then treated with 2 ml. of ethyl acetate. Sufficient dilute hydrochloric acid was then added to decompose the complex, and the layers were separated. The ether layer was washed with dilute hydrochloric acid, sodium bicarbonate solution, and water. Evaporation of the ether layer and crystallization of the residue from benzene–pentane gave 510 mg. (88%) of product, m.p. 163–164°. For analysis, a small sample was recrystallized twice from benzene–pentane, m.p. 164.2–164.6°.

Anal. Calcd. for $C_{20}H_{24}O$: C, 85.67; H, 8.63. Found: C, 85.89; H, 8.71.

2-Tosyloxy[4.4]paracyclophane (XXIX).—Alcohol XXVIII, 290 mg., was dissolved in 1.4 ml. of dry pyridine, and the solution was cooled in an ice-bath. To this cooled solution was added 240 mg. of *p*-toluenesulfonyl chloride in 0.6 ml. of dry pyridine. The resulting solution was allowed to stand at 0° overnight, and then an additional hour at room temperature. The reaction mixture was diluted with ether, and was then washed consecutively with dilute sulfuric acid, sodium bicarbonate solution, and water. The ether layer was concentrated and diluted with pentane to give 260 mg. (58%) of product, m.p. 130° dec. For analysis, a small sample was recrystallized 4 times from ether–pentane, m.p. 119° dec.

Anal. Calcd. for $C_{27}H_{30}O_3S$: C, 74.62; H, 6.96. Found: C, 74.86; H, 6.69.

Evaporation of the mother liquors from which the tosylate was first isolated gave 110 mg. (38%) of crude starting material, m.p. 130–140°.

***trans*-2,3-Dehydro[4.4]paracyclophane (XXX).**—Tosylate XXIX, 195 mg., and 3 ml. of 1 *M* potassium *t*-butoxide in *t*-butyl alcohol were mixed and refluxed under nitrogen for 1 hour. The reaction mixture was cooled, diluted with water, and extracted with ether. The ether extract was washed twice with water and dried. Evaporation of the ether and chromatography of the residue on alumina gave 65 mg. (55%) of crude product, m.p. 110–114°. For analysis, a small sample was recrystallized 3 times from ethanol-water, m.p. 121.8–122.5°.

Anal. Calcd. for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.53; H, 8.45.

Catalytic Hydrogenation of *trans*-2,3-Dehydro[4.4]paracyclophane (XXX).—Olefin XXX, 5.0 mg., 1 mg. of platinum oxide and 15 ml. of ethanol were mixed and hydrogenated. The ethanol was then filtered, concentrated to 1 ml., diluted slightly with water, and cooled to give 4.0 mg. (80%) of [4.4]paracyclophane(X), m.p. 141–144°. Admixture of this material with an authentic sample of X did not depress the melting point.

2,3-Dihydroxy[4.4]paracyclophane (XXVI).—Acetonide XXIII, 2.90 g., was heated with aqueous dioxane–hydrochloric acid on a steam-bath for half an hour. The reaction mixture was cooled and extracted with carbon tetrachloride. Evaporation of the carbon tetrachloride layer and crystallization of the residue from benzene–hexane gave 2.05 g. (80%) of product, m.p. 191–193°. For analysis, a small sample was recrystallized 3 times from benzene–hexane, m.p. 194.2–195.0°.

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

Anal. Calcd. for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16. Found: C, 80.90; H, 7.97.

2,3-Diacetoxy[4.4]paracyclophane (XXVII).—Diol XXVI, 1.0 g., 4 g. of acetic anhydride and 10 ml. of pyridine were mixed and refluxed for 4 minutes. The reaction mixture was cooled, poured into 50 ml. of ice-water, and filtered. The solid was washed well with dilute hydrochloric acid and water, and then chromatographed to give 1.23 g. (96%) of product, m.p. 151–152°. For analysis, a small sample was crystallized from benzene–pentane, m.p. 152.3–153.4°. The infrared spectrum of this material in chloroform showed a strong band at 1728 cm.$^{-1}$, but showed none in the 3400 cm.$^{-1}$ region.

Anal. Calcd. for $C_{24}H_{28}O_4$: C, 75.76; H, 7.42. Found: C, 75.87; H, 7.42.

1,2,3,4-Dehydro[4.4]paracyclophane (XVII).—Diacetate XXVII, 450 mg., was heated in a small test-tube supplied with dry, oxygen-free nitrogen at 500° for 25 seconds. The reaction mixture was cooled rapidly, diluted with benzene, and adsorbed on a column of neutral alumina of activity *ca.* IV.[15] Elution of the column with pentane gave 40 mg. (13%) of product, m.p. 104–111°. Elution of the column with 25% ether–pentane gave 225 mg. (50%) of starting diacetate. For analysis, a small sample of olefin XVII was recrystallized 3 times from ethanol–water, m.p. 115.8–116.5°.

Anal. Calcd. for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.21; H, 7.88.

A maleic anhydride adduct of this compound could not be prepared.

Catalytic Hydrogenation of 1,2,3,4-Dehydro[4.4]paracyclophane (XVII).—Diene XVII, 33 mg., 2 mg. of platinum oxide and 15 ml. of ethanol were mixed and hydrogenated. The ethanol was filtered, concentrated, diluted with water, and cooled to give 25 mg. (75%) of [4.4]paracyclophane(X), m.p. 144–146°. One crystallization of this material raised the melting point to 146.2–147.2°, undepressed on admixture with an authentic sample of X.

1,4,11-Tribromo[4.4]paracyclophane.—A mixture of 1.0 g. of [4.4]paracyclophane (X), 1.6 g. of N-bromosuccinimide, 100 ml. of carbon tetrachloride, and a small quantity of benzoyl peroxide was refluxed for 2 hours. The reaction mixture was then cooled, filtered, and the filtrate was successively washed with sodium bicarbonate solution and water, dried and evaporated. Repeated crystallization of the residue gave 500 mg. (29%) of crude product, m.p. 212°. For analysis, a small sample was twice recrystallized from benzene–hexane, m.p. 217–219°.

Anal. Calcd. for $C_{20}H_{21}Br_3$: C, 47.93; H, 4.22. Found: C, 47.41; H, 4.32.

Attempted Synthesis of 1,2,3,4,11,12-Dehydro[4.4]paracyclophane.—All attempts to eliminate the elements of hydrogen bromide from tribromide (see above) with potassium *t*-butoxide in *t*-butyl alcohol and with pyridine failed. With dimethylamine, a small quantity of partially-eliminated material could be isolated as follows. Tribromide, 1.2 g., was heated with dimethylamine (containing a small amount of benzene) in a sealed tube at 110° for 2 days. The reaction mixture was evaporated, treated with aqueous potassium hydroxide, and extracted with ether. The ether layer was evaporated and the residue was adsorbed on a column of neutral alumina of activity I.[15] Elution of the column with 1% ether–pentane gave a small quantity of monobromide, m.p. 150°. Elution of the column with eluants of increasing ether content gave only mixtures. For analysis, the monobromide was twice recrystallized from ethanol–water, m.p. 150.4–152.0°. The analysis is approximately correct for $C_{20}H_{19}Br$. The material has a strong ultraviolet absorption band at 261 mμ.

Anal. Found: C, 69.53; H, 5.22.

1,4,11,14-Tetrabromo[4.4]paracyclophane (XXXII).—[4.4]Paracyclophane(X), 2.0 g., 5.8 g. of N-bromosuccinimide, 150 ml. of carbon tetrachloride and a small quantity of benzoyl peroxide were mixed and refluxed for 2 hours. The reaction mixture was concentrated, diluted with pentane, and filtered. The solid was washed with several portions of hot water and thoroughly dried to give 4.3 g. (98%) of crude tetrabromide XXXII. The relative insolubility of this compound made purification and analysis undesirable.

1,2,3,4,11,12,13,14-Dehydro[4.4]paracyclophane (XXXI).—Tetrabromide XXXII, 6.0 g., 20 ml. of benzene and 100 ml. of dimethylamine were placed in an autoclave and heated at 140° for 24 hours. The reaction mixture was evaporated, diluted with aqueous sodium hydroxide, and extracted with ether. The ether layer was evaporated and the residue was adsorbed on a large column of neutral alumina of activity I.[15] Elution of the column with pentane, evaporation of the eluate, and crystallization of the residue from ethanol–water gave 96 mg. (3.6%) of product, m.p. 128–132°. For analysis, a small sample was recrystallized 3 times from ethanol–water, m.p. 136.0–136.8°.

Anal. Calcd. for $C_{20}H_{16}$: C, 93.71; H, 6.29. Found: C, 93.65; H, 6.00.

Catalytic Hydrogenation of 1,2,3,4,11,12,13,14-Dehydro[4.4]paracyclophane (XXXI).—Tetraolefin, XXXI, 31 mg., 10 mg. of platinum oxide and 20 ml. of ethanol were mixed and hydrogenated. The ethanol was filtered, concentrated, diluted with water, and cooled to give 24 mg. (77%) of [4.4]paracyclophane(X), m.p. 146–147°. Admixture of this material with an authentic sample of X did not depress the melting point.

1-(4-Methylphenyl)-4-phenyl-1-butanone.—Magnesium, 24.5 g., was placed in the usual Grignard apparatus with 100 ml. of ether. A solution of 199 g. of γ-phenylpropyl bromide in 150 ml. of ether was added to the refluxing reaction flask over a period of 2 hours, and the resulting solution was refluxed an additional half hour. *p*-Tolunitrile, 100 g., was then added over a period of half an hour, and the solution was refluxed for 6 hours. The cooled reaction mixture was hydrolyzed with dilute hydrochloric acid, and the ether layer was washed successively with dilute hydrochloric acid, sodium bicarbonate solution and water. The ether layer was dried and flash distilled through a Claisen flask to give a small forerun, b.p. 90–170° (2 mm.), and 133 g. (65%) of product, b.p. 179–181° (2 mm.). The product slowly crystallized at room temperature, m.p. 37–38°. For analysis, a small sample was recrystallized 3 times from benzene–pentane, m.p. 38.6–39.2°.

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.44; H, 7.77.

1-(4-Methylphenyl)-4-phenylbutane.—The ketone, 1-(4-methylphenyl)-4-phenyl-1-butanone, 128 g., was dissolved in a solution of 50 g. of hydrazine and 70 g. of potassium hydroxide in 700 ml. of diethylene glycol, and the resulting solution was refluxed for 1 hour. At the end of this time, the reflux condenser was removed until the temperature of the boiling liquid reached 200°. The condenser was replaced, and the mixture refluxed overnight. The reaction mixture was cooled, diluted with 2.5 l. of water, and extracted with ether. The ether extract was dried and distilled through a short Vigreux column to give 109 g. (90%) of product, b.p. 195–196° (20 mm.), n^{25}D 1.5460. For analysis, a small sample was chromatographed and redistilled.

Anal. Calcd. for $C_{17}H_{20}$: C, 91.01; H, 8.99. Found: C, 91.08; H, 8.94.

1-(4-Methylphenyl)-4-(4-acetylphenyl)-butane.—1-(4-Methylphenyl)-4-phenylbutane, 23 g., 10.3 g. of acetic anhydride and 100 ml. of tetrachloroethane were mixed and cooled in an ice–salt-bath. Aluminum chloride, 31 g., was then added in small portions over a period of 1 hour, and the resulting mixture was stirred at −5° for 4 hours. The reaction mixture was hydrolyzed successively with ice and dilute hydrochloric acid, and the tetrachloroethane layer was washed with dilute hydrochloric acid, sodium bicarbonate solution, and water. The dried tetrachloroethane layer was flash distilled through a Claisen flask to give a small forerun, b.p. 145–150° (1.5 mm.), and crude product, b.p. 200–210° (1.5 mm.). The high-boiling distillate, which solidified on standing, was crystallized from benzene–pentane to give 15 g. (55%) of product, m.p. 50–52°. For analysis, a small sample was recrystallized 3 times from benzene–pentane, m.p. 56.6–57.2°.

Anal. Calcd. for $C_{19}H_{22}O$: C, 85.67; H, 8.33. Found: C, 85.75; H, 8.20.

1-(4-Methylphenyl)-4-(4-carboxymethylphenyl)-butane.—1-(4-Methylphenyl)-4-(4-acetylphenyl)-butane, 10.3 g., 1.9 g. of sulfur and 35 ml. of morpholine were mixed and refluxed overnight. The hot mixture was poured into 65 ml. of 95% ethanol and cooled to give 12.1 g. (81%) of the thiomorpholide of the desired acid, m.p. 108.4–109.8°. For analysis, a small sample was recrystallized 4 times from ethanol–water, m.p. 110.2–111.2°.

Anal. Calcd. for $C_{23}H_{29}ONS$: C, 75.16; H, 7.95. Found: C, 75.23; H, 7.75.

The thiomorpholide, 9.7 g., 5.2 g. of potassium hydroxide, and 40 ml. of ethanol were mixed and refluxed overnight. The reaction mixture was concentrated, diluted with water, and cautiously acidified at 0° with concentrated hydrochloric acid. The precipitate was collected, dried in a vacuum oven, and crystallized from ethanol–water to give 6.7 g. (92%) of the acid, m.p. 117–118°. For analysis, a small sample was recrystallized 3 times from ethanol–water, m.p. 119.4–120.0°.

Anal. Calcd. for $C_{19}H_{22}O_2$: C, 80.81; H, 7.85; Found: C, 80.70; H, 8.10.

1-(4-Methylphenyl)-4-(4-acetonylphenyl)-butane (XXXIII).—A solution of 3.7 ml. of methyl iodide in 15 ml. of ether was added slowly to a cooled mixture of 370 mg. of lithium ribbon in 10 ml. of ether. The mixture was then refluxed until solution of the lithium was complete (*ca.* 2 hours). The resulting solution was slowly added with vigorous stirring to a solution of 3.0 g. of 1-(4-methylphenyl)-4-(4-carboxymethylphenyl)-butane in 150 ml. of ether. The reaction mixture was stirred under reflux an additional half-an-hour, cooled in an ice-bath, and decomposed successively with water and dilute hydrochloric acid. The ether layer was washed successively with sodium bicarbonate solution and water, dried, and evaporated. The residue was chromatographed on neutral alumina to give 1.3 g. (43%) of product, m.p. 65–66°. For analysis, a small sample was recrystallized 3 times from benzene–pentane, m.p. 66.0–66.6°.

Anal. Calcd. for $C_{20}H_{24}O$: C, 85.67; H, 8.63. Found: C, 85.93; H, 8.45.

1,2,9,10,17,18-Hexabromo[2.2.2]paracyclophane (IV).—[2.2.2]Paracyclophane (II), 3.1 g., 10.8 g. of N-bromosuccinimide, 300 ml. of carbon tetrachloride and a small quantity of benzoyl peroxide were mixed and refluxed overnight. The reaction mixture was filtered, concentrated and diluted with pentane to give 7.2 g. (91%) of crude product, m.p. 250–280°. For analysis, a small sample was chromatographed and crystallized from benzene–hexane to give a discrete isomer, m.p. 303° dec. The ultraviolet spectrum of this compound exhibited a strong band at 253 mμ (ε 33,000).

Anal. Calcd. for $C_{24}H_{18}Br_6$: C, 36.68, H, 2.31. Found: C, 36.61; H, 2.43.

1,2,9,10,17,18-Dehydro[2.2.2]paracyclophane(III).–Hexabromide IV, 4.5 g., 20 g. of zinc activated with ammonium chloride and 600 ml. of ethanol were mixed and refluxed in an atmosphere of nitrogen overnight. The reaction mixture was filtered to remove zinc, diluted with water, and filtered. The solid was adsorbed on a column of neutral alumina of activity I[15] and eluted with pentane to give 820 mg. (47%) of product, m.p. 128–131°. For analysis, a small sample was repeatedly crystallized from ethanol-water, m.p. 136.0–136.8°.

Anal. Calcd. for $C_{24}H_{18}$: C, 94.08; H, 5.92. Found: C, 94.08; H, 6.06.

Catalytic Hydrogenation of 1,2,9,10,17,18-Dehydro-[2.2.2]paracyclophane (III).—Triolefin III, 100 mg., 15 mg. of platinum oxide and 50 ml. of ethanol were mixed and hydrogenated. The ethanol was filtered, concentrated, diluted with water, and cooled to give 72 mg. (71%) of [2.2.2]paracyclophane (II), m.p. 162–164°. One crystallization of this material raised the melting point to 165.0–166.6°, undepressed on admixture with an authentic sample of II.

Perhydro[2.2.2]paracyclophane (V).—[2.2.2]Paracyclophane (II), 1.0 g., 120 mg. of platinum oxide and 80 ml. of acetic acid were mixed and hydrogenated. The acetic acid was filtered and evaporated to give 750 mg. (71%) of product, m.p. 174.2–175.6°. For analysis, a small sample was recrystallized twice from ethanol, m.p. 175.2–176.0°.

Anal. Calcd. for $C_{24}H_{42}$: C, 87.19; H, 12.81. Found: C, 87.09; H, 12.72.

Treatment of Perhydro[2.2.2]paracyclophane (V) with Palladium - Carbon.—Perhydro[2.2.2]paracyclophane(V), 480 mg., was heated with 50 mg. of palladium–carbon at 310°. The reaction mixture was cooled, diluted with benzene, and filtered. Evaporation of the benzene and crystallization of the residue from ethanol gave 350 mg. (78%) of [2.2.2]paracyclophane (II), m.p. 164–166°. Admixture of this material with an authentic sample of II did not depress the melting point.

LOS ANGELES, CALIF.

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

Macro Rings. XX. Transannular Effects in π-π-Complexes[1]

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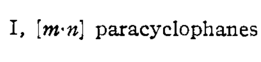
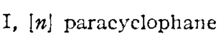
The ultraviolet absorption spectra of one-to-one tetracyanoethylene–paracyclophane charge-transfer complexes have been examined, and compared to those of open-chain models. The absorption band that occurs at the longest wave length varies with the structure of the hydrocarbon part of the 21 paracyclophane complexes studied, and ranges between extremes of 599 mμ for [3.3]paracyclophane (I, $m = n = 3$) to 476 mμ for [4.4]paracyclophane, (I, $m = n = 4$) in dichloromethane as solvent. Open-chain model compounds possess spectra that vary from 470 to 460 mμ in the position of λ_{max}. The color of the paracyclophane complexes in solution varies from yellow-orange to blue. The positions of λ_{max} (long wave length) for the complex of [3.4]paracyclophane (I, $m = 4$, $n = 3$) range between the limits of 540 mμ in chloroform to 450 mμ in *t*-butyl alcohol as the solvating power and acid-base character of the solvent is changed. A number of solid complexes were isolated and characterized. The differences in spectra between the different complexes and between the same complexes in different solvents is interpreted in terms of the ability of the non-complexed ring to delocalize positive charge in the ground and excited states of the complex. The infrared spectrum of the complex of [3.4]paracyclophane-tetracyanoethylene is different in important respects from those of either component taken separately.

In earlier papers of this series, the preparation of 18 paracyclophanes of general structure I, and 3 of general structure II has been reported.[2] The spectra[3] and reactivity[2] of compounds of structure I vary systematically as the distance between the two benzene rings is altered, and these effects have been interpreted in terms of transannular interaction of the π-electron clouds of the two aromatic nuclei with one another.



I, [*m*·*n*] paracyclophanes



II, [*n*] paracyclophanes

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[2] The previous paper of the series is D. J. Cram and K. Dewhirst, THIS JOURNAL, **81**, 0000 (1959).

[3] (a) D. J. Cram, N. L. Allinger and H. Steinberg, *ibid.*, **76**, 6132 (1954); (b) D. J. Cram and M. F. Antar, *ibid.*, **80**, 3103 (1958).