was sublimed at 230° (6×10^{-4} mm.) to give a white powder, 6,16-dicarboxy[4.4]paracyclophane (XXVI) (0.306 g., 76%). For analysis, the material was crystallized from glacial acetic acid to give tiny white prisms, m.p. 297–302° (slight decomposition from 285°).

Anal. Calcd. for $C_{22}H_{24}O_4$: C, 74.98; H, 6.86. Found: C, 74.94; H, 6.92.

Clemmensen Reduction of 6-Ethyl-9-acetyl[4.4]paracyclophane (XX).—Amalgamated zinc was prepared from mossy zinc (5 g.). 6-Ethyl-9-acetyl[4.4]paracyclophane (0.096 g., 0.000287 mole) dissolved in glacial acetic acid (10 ml.) was added, followed by concentrated hydrochloric acid (10 ml.), and the mixture was heated at reflux for 30 hours, with addition of portions of concentrated hydrochloric acid (3 ml.) at 8-hour intervals. The mixture was cooled, poured into water, and extracted with ether. The ether solution was washed with water, sodium bicarbonate solution, and again with water. The solution was dried and concentrated to give a white solid which was absorbed on a column of neutral activity I alumina (20 g.) made up in pentane. 6,9-Diethyl[4.4]paracyclophane (0.062 g., 60%) was eluted with pentane as a white solid, m.p. 108.5–111°. Two crystallizations of the material from 95% ethanol gave fat white needles, m.p. 109.9–111.6°.

Anal. Calcd. for $C_{24}H_{32}$: C, 89.93; H, 10.07. Found: C, 89.73; H, 10.00.

Clemmensen Reduction of 6,16-Diacetyl[4.4]paracyclophane.—Amalgamated zinc was prepared from mossy zinc (8 g.). 6,16-Diacetyl[4.4]paracyclophane (0.110 g., 0.000316 mole) dissolved in glacial acetic acid (10 ml.) was added, followed by concentrated hydrochloric acid (10 ml.). The mixture was refluxed for 75 hours, with addition of portions of concentrated hydrochloric acid (2.5 ml.) at 8-hour intervals. The mixture was cooled, poured into water, and extracted with ether. The ether solution was washed with water, sodium bicarbonate solution, and again with water. The solution was dried and concentrated to give a colorless oil which was catalytically reduced in ethanol. There was little or no hydrogen absorbed. The ethanol solution was poured into water, and the mixture was extracted with ether. The ether solution was washed with water and dried. The solution was concentrated to give an oil which was adsorbed on a column of neutral activity I alumina (20 g.) made up in pentane. 6,16-Diethyl[4.4]-paracyclophane (0.057 g., 56%) was eluted with pentane as a colorless liquid. For analysis, the liquid was distilled at 115° (bath temperature) (0.5 mm.).

Anal. Calcd. for $C_{24}H_{32}$: C, 89.93; H, 10.07. Found: C, 89.65; H, 10.18.

Clemmensen Reduction of 6,17-Diacetyl[4.4]paracyclophane.—Amalgamated zinc was prepared from mossy zinc (5 g.). 6,17-Diacetyl[4.4]paracyclophane (0.110 g., 0.000316 mole) dissolved in glacial acetic acid (10 ml.) was added, followed by concentrated hydrochloric acid (10 ml.). The mixture was heated at reflux for 30 hours, with addition of portions of concentrated hydrochloric acid (3 ml.) at 8-hour intervals. The mixture was cooled, poured into water, and extracted with ether. The ether solution was washed with water, sodium bicarbonate solution, and again with water. The solution was dried and concentrated to give an oil which was adsorbed on a column of neutral activity I alumina made up in pentane. 6,17-Diethyl[4.4]paracyclophane (0.054 g., 54%) was eluted with pentane as a colorless liquid. For analysis, the liquid was distilled at 110° (bath temperature) (0.5 mm.).

Anal. Calcd. for $C_{24}H_{32}$: C, 89.93; H, 10.07. Found: C, 89.75; H, 10.02.

LOS ANGELES 24, CALIFORNIA

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

Macro Rings. XV. The Synthesis and Properties of Six New Paracyclophanes Carrying One Methylene in One of the Bridges[1]

BY DONALD J. CRAM AND M. FARID ANTAR

RECEIVED JANUARY 14, 1958

A series of six homologous paracyclophanes (I) have been prepared in which one of the two bridges carries one methylene and the other, 7, 8, 9, 10, 11 and 12 methylene groups. The smallest cycle preparable through use of the acyloin reaction on diester carrying *two aromatic rings* was [1.8]paracyclophane (I, $m = 1$, $n = 8$). The smallest cycle preparable through use of the acyloin reaction on diester carrying *two cyclohexane rings* was the [1.7]paracyclophane. The benzene rings of the latter compound are probably bent from their normal planar geometry. The ultraviolet absorption spectra of this series of compounds exhibit an even progression of λ_{max} toward longer wave lengths as the benzene rings are drawn toward one another, the smallest cycle possessing an entirely different spectrum from that of the open chain model. These spectral changes are attributed to transannular interactions between the π-electrons of the two benzene rings, the effects becoming more serious as the π-orbitals of each ring are pressed more and more into each other's environment.

The preparation,[2] spectral properties[2a,e] and reactions[3,4] of the more symmetrical paracyclophanes (I with n or m = 2 to 6) have been reported in earlier papers of this series. The sandwich-like geometry of the aromatic portions of these more symmetrical cycles places the π-orbitals of each ring end to end, as indicated in II. This paper is concerned with the construction and properties of compounds shaped more like clams (III), in which at one end of the molecule the π-orbitals of the two benzene rings are orthogonal to one another. The synthesis of III with $n = 8$ has been previously reported.[2d]

Synthesis.—All of the cycles except [1.7]paracyclophane were prepared by the general synthetic sequence outlined in Chart I. Table I reports the physical constants and analyses of the compounds involved, and the Experimental reports typical procedures employed. Compounds XXII, XXVIII, XXXIII, XXXVIII, XLIV, XLV and XLVI have been reported previously. In some cases intermediates (*e.g.*, XI) were not characterized but were used directly in the next step. These syntheses were greatly facilitated by the interesting fact that diphenylmethane can be acylated to give either mono- or bis-substituted product in good yield, depending on the number of moles of acylating agent employed. Clearly an acyl group

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(1) This work was supported by a generous grant from the Upjohn Co.

(2) (a) D. J. Cram and H. Steinberg, THIS JOURNAL, **73**, 5691 (1951); (b) D. J. Cram and N. L. Allinger, *ibid.*, **76**, 726 (1954); (c) N. L. Allinger and D. J. Cram, *ibid.*, **76**, 2362 (1954); (d) J. Abell and D. J. Cram, *ibid.*, **76**, 4406 (1954); (e) D. J. Cram, N. L. Allinger and H. Steinberg, *ibid.*, **76**, 6132 (1954).

(3) (a) D. J. Cram and R. W. Kierstead, *ibid.*, **77**, 1186 (1955); (b) D. J. Cram and N. L. Allinger, *ibid.*, **77**, 6289 (1955);

(4) D. J. Cram and R. Reeves, *ibid.*, **80**, 3094 (1958).

CHART I

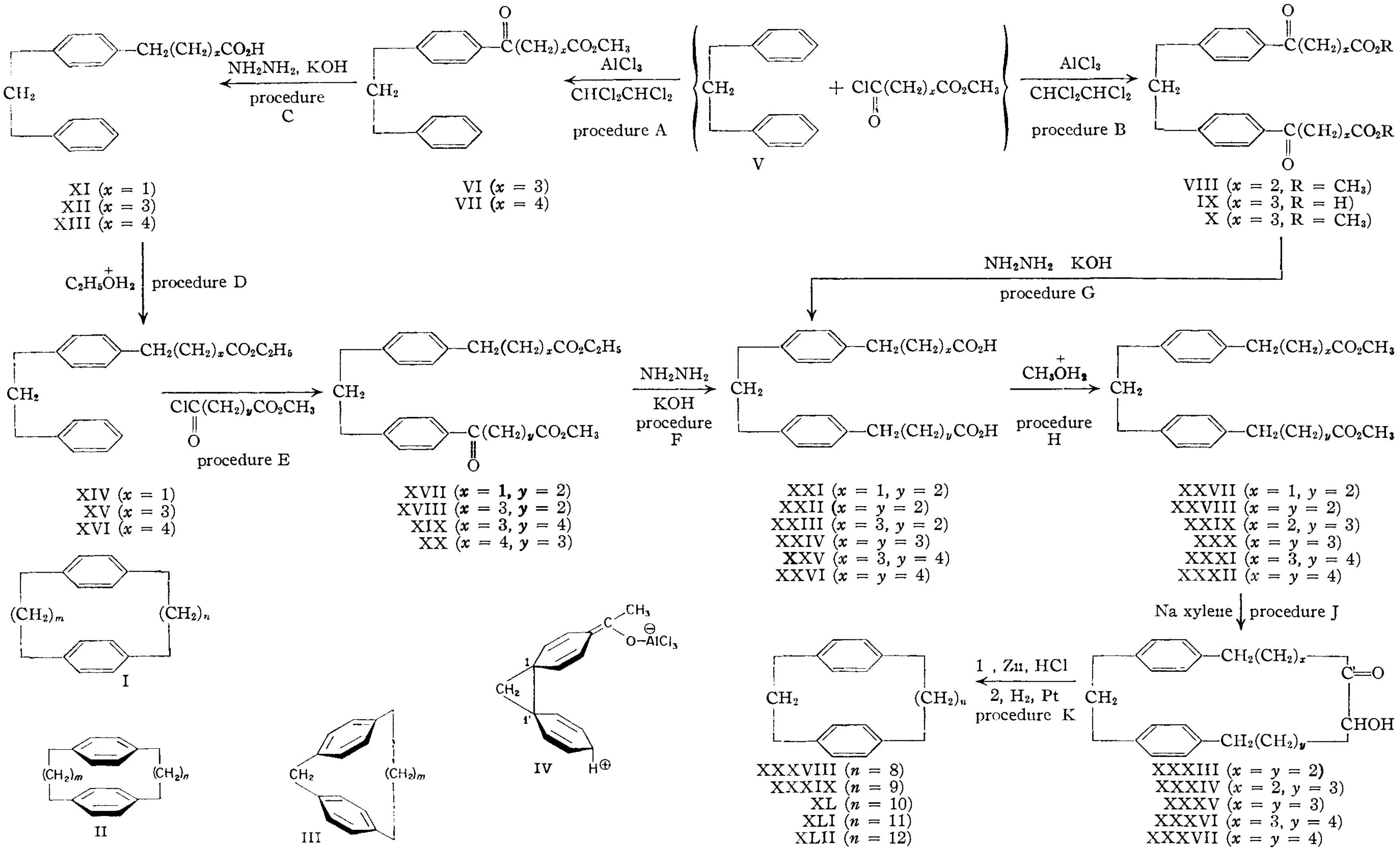
—CH2(CH2)xCO2H
CH2
NH2NH2, KOH
procedure C
XI (x = 1)
XII (x = 3)
XIII (x = 4)
—C(CH2)xCO2CH3
O
AlCl3
CHCl2CHCl2
procedure A
VI (x = 3)
VII (x = 4)
V
+ ClC(CH2)xCO2CH3
AlCl3
CHCl2CHCl2
procedure B
—C(CH2)xCO2R
VIII (x = 2, R = CH3)
IX (x = 3, R = H)
X (x = 3, R = CH3)
NH2NH2 KOH
procedure G
C2H5OH2+ procedure D
—CH2(CH2)xCO2C2H5
ClC(CH2)yCO2CH3
procedure E
XIV (x = 1)
XV (x = 3)
XVI (x = 4)
—C(CH2)yCO2CH3
XVII (x = 1, y = 2)
XVIII (x = 3, y = 2)
XIX (x = 3, y = 4)
XX (x = 4, y = 3)
NH2NH2
KOH
procedure F
—CH2(CH2)yCO2H
XXI (x = 1, y = 2)
XXII (x = y = 2)
XXIII (x = 3, y = 2)
XXIV (x = y = 3)
XXV (x = 3, y = 4)
XXVI (x = y = 4)
CH3OH2+
procedure H
—CH2(CH2)xCO2CH3
—CH2(CH2)yCO2CH3
XXVII (x = 1, y = 2)
XXVIII (x = y = 2)
XXIX (x = 2, y = 3)
XXX (x = y = 3)
XXXI (x = 3, y = 4)
XXXII (x = y = 4)
Na xylene procedure J
—CH2(CH2)x—
C=O
CHOH
—CH2(CH2)y—
XXXIII (x = y = 2)
XXXIV (x = 2, y = 3)
XXXV (x = y = 3)
XXXVI (x = 3, y = 4)
XXXVII (x = y = 4)
1, Zn, HCl
2, H2, Pt
procedure K
(CH2)n
XXXVIII (n = 8)
XXXIX (n = 9)
XL (n = 10)
XLI (n = 11)
XLII (n = 12)
(CH2)m
(CH2)n
I
II
III
CH3
C
O–AlCl3
1
1'
H⊕
IV

TABLE I

YIELD AND ANALYTICAL DATA CONCERNING PARACYCLOPHANE SYNTHESES

Compound	Prep. proc.	Yield, %	M.p., °C.	Crystn. solvent	B.p.		n^{25}_D	Formula	Carbon, %		Hydrogen, %	
					°C.	Mm.			Calcd.	Found	Calcd.	Found
VI	A	80	41–42	Pet. ether	.....	..	....	$C_{19}H_{20}O_3$	77.00	76.89	6.80	6.53
VII	A	70	52.5–54	Pet. ether	.....	..	....	$C_{20}H_{22}O_3$	77.39	77.67	7.14	7.39
VIII	B	70	93–94	Benz.-hex.	.....	..	....	$C_{23}H_{24}O_6$	69.68	69.91	6.10	5.94
IX	B	71	97.5–99.5	Benz.-hex.	.....	..	....	$C_{23}H_{24}O_6$	69.68	69.86	6.10	6.14
X	B	62	67.5–68.3	Benz.-hex.	.....	..	....	$C_{27}H_{32}O_6$	71.66	71.56	7.13	7.16
XII	C	90	70–71	Ether	.....	..	....	$C_{18}H_{20}O_2$	80.81	81.54	7.51	7.74
XIII	C	95	68.5–69.7	Pet. ether	.....	..	....	$C_{19}H_{22}O_2$	80.56	80.00	7.85	7.75
XIV	D	66	....	......	153–154	0.2	1.5473	$C_{18}H_{20}O_2$	80.56	80.82	7.51	7.54
XV	D	92	....	......	202	1.7	1.5368	$C_{20}H_{24}O_2$	81.04	80.84	8.16	7.91
XVI	D	90	....	......	205–206	1	1.5336	$C_{21}H_{26}O_2$	81.25	81.51	8.44	8.14
XVII	E	71	....	......	273–275	1.5	1.5498	$C_{23}H_{26}O_5$	72.23	72.15	6.85	6.76
XVIII	E	63	40–41.8	Benz.-hex.	.....	..	....	$C_{25}H_{30}O_5$	73.14	73.26	7.37	7.51
XIX	E	60	....	......	270–280	1.5	1.5379	$C_{27}H_{34}O_5$	73.94	74.08	7.82	7.91
XX	E	65	45.2–46.5	Pet. ether	.....	..	....	$C_{27}H_{34}O_5$	73.94	73.93	7.82	7.66
XXI	F	91	162.3–163.7	Ether	.....	..	....	$C_{20}H_{22}O_4$	73.60	73.48	6.79	6.66
XXIII	F	90	146–147.2	Benz.-hex.	.....	..	....	$C_{22}H_{26}O_4$	74.55	74.29	7.39	7.63
XXIV	G	77	138.5–140	Benz.-hex.	.....	..	....	$C_{23}H_{28}O_4$	74.97	74.57	7.80	7.77
XXV	F	70	123.5–124.5	Ether	.....	..	....	$C_{24}H_{30}O_4$	75.36	75.50	7.91	7.82
XXVI	G	90	151.4–152.3	Benz.-hex.	.....	..	....	$C_{25}H_{32}O_4$	75.72	75.32	8.13	8.05
XXVII	H	89	....	......	236–237	1.2	1.5394	$C_{22}H_{26}O_4$	74.55	74.44	7.39	7.30
XXVIII	H	85	....	......	275–276	1	1.5345	$C_{23}H_{28}O_4$	74.97	74.92	7.66	7.44
XXIX	H	90	....	......	248–250	0.5	1.5332	$C_{24}H_{30}O_4$	75.36	75.50	7.91	7.71
XXX	H	86	....	......	256–258	1	1.5295	$C_{25}H_{32}O_4$	75.72	75.81	8.13	7.90
XXXI	H	54	....	......	243–245	0.2	1.5264	$C_{26}H_{34}O_4$	76.06	76.16	8.34	8.37
XXXII	H	95	....	......	248–250	0.2	1.5248	$C_{27}H_{36}O_4$	76.38	76.45	8.55	8.59
XXXIII	J	28	121.3–122.6	Wat.-meth.	.....	..	....	$C_{21}H_{24}O_2$	81.78	81.97	7.84	7.86
XXXIV	J	46	96.5–98.3	Meth.	.....	..	....	$C_{22}H_{26}O_2$	81.95	82.21	8.13	8.23
XXXV	J	62	119–120.3	Meth.	.....	..	....	$C_{23}H_{28}O_2$	82.10	82.31	8.39	8.45
XXXVI	J	51	95.6–96.3	Meth.	.....	..	....	$C_{24}H_{30}O_2$	82.24	82.31	8.63	8.45
XXXVII	J	80	78.9–79.8	Meth.	.....	..	....	$C_{25}H_{32}O_2$	82.37	82.15	8.85	8.83
XXXVIII	K	93	119.5–121	Meth.	.....	..	....	$C_{21}H_{26}$	90.59	90.64	9.41	9.16
XXXIX	K	80	85.2–86	Meth.	.....	..	....	$C_{22}H_{28}$	90.35	90.10	9.65	9.73
XL	K	82	63.9–64.8	Meth.	.....	..	....	$C_{23}H_{30}$	90.13	89.91	9.87	9.89
XLI	K	70	77.8–78.6	Meth.	.....	..	....	$C_{24}H_{32}$	89.94	89.94	10.06	9.97
XLII	K	90	49.8–50.7	Meth.	.....	..	....	$C_{25}H_{34}$	89.75	89.70	10.25	10.19
XLIII	A	83	41.8–43.2	Wat.-meth.	.....	..	....	$C_{16}H_{16}O$	85.68	85.62	7.19	7.20
XLVII	M	98	....	......	214–216	1	1.4817	$C_{22}H_{38}O_4$	72.09	72.01	10.45	10.23
XLIX	K	..[a]	78.4–80	Meth.	.....	..	....	$C_{20}H_{36}$	86.88	87.10	13.12	13.23
L	N	2	76.5–77.2	Meth.	.....	..	....	$C_{20}H_{24}$	90.85	90.80	9.15	9.11

[a] See Experimental.

in the *p*-position of one ring deactivates the second ring toward electrophilic attack by acylating agent enough so that the rates of acylation of non-substituted and monosubstituted material are enough separated to permit good yields of either product to be obtained. This behavior contrasts with that of bibenzyl, which when treated with one mole of acylating agent produces a mixture of non-, mono- and di-acylated material in proportions which indicate that each ring underwent substitution at a rate essentially independent of the presence of a substituent in the second ring.[5] Higher homologs such as 1,3-diphenylpropane behave similarly to bibenzyl.[2e] Thus this unique character is associated with the smallest homolog of the diphenylalkanes and is probably due to transannular deactivating influence of an aluminum chloride-complexed acyl group in one ring on the second ring. This transannular effect was also observed in the acylation of [2.2]- and [4.4]paracyclophane,[3a,b] and might be due to the distribution of positive charge in both rings, as indicated in structure IV. The C-1 to C-1′ distance is about 2.5 Å., which is well within the normal van der Waals distance which separates the planes of aromatic nuclei in crystals.[6] Apparently the amount of charge in the non-acylated ring is not sufficient to prevent the second ring from acylating in the presence of excess reagent, nor from completely counteracting the *para*-directing ability of the methylene group in this second ring.

The acyloin ring closure failed to work when the bridge being formed carried less than eight carbon atoms. As expected the yield drops as the length of the bridge spanning the two aromatic nuclei decreases. With ten carbons in the bridge, the yield was 62%, with nine carbons, 46%, with eight carbons, 28%, with seven carbons, 0%. As indicated in Chart II, the ring closure did occur to give a seven-carbon bridge in minute yield when the two benzene rings were converted into cyclohexane

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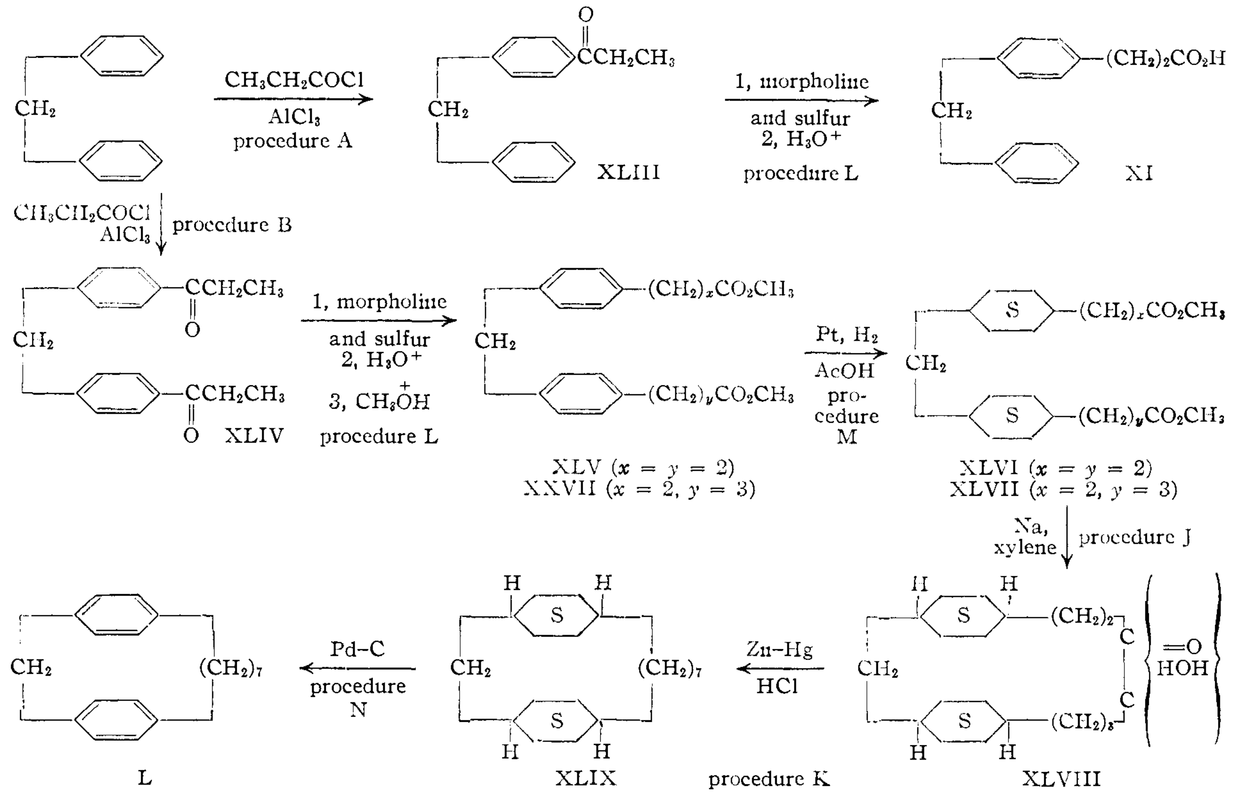
[5] D. J. Cram and H. Steinberg, unpublished results.

[6] J. M. Robertson, "Organic Crystals and Molecules," Cornell University Press, Ithaca, N. Y., 1953, pp. 157, 206, 270 and 274.

CHART II



rings. Although all three isomers of diester XLVII (see Chart II) probably were produced[2c] during the catalytic reduction, molecular models indicate that only the predominating *cis,cis* isomer[2c] could have undergone ring closure. When the same procedure was applied to the synthesis of [1,6]paracyclophane,[3b] the acyloin ring closure of diester XLVI failed to yield any cycle. As was observed earlier[2c,e] with the lower homologs, in the aromatization of XLIX, the yield was poor (2%), and a considerable amount of ring-ruptured product seemed to be produced whose separation from the desired cycle proved difficult.

Spectra.—Figure 1 records the ultraviolet absorption spectra of the six paracyclophanes along with that of the two open chain models, one being a *p,p'*-dialkyldiphenylmethane and the other, a *p,p'*-dialkyl-1,6-diphenylhexane. A small but nonetheless distinguishable difference exists between the spectra of these two models. Of the two models, that carrying only one methylene group separating the two benzene rings possesses $\lambda_{\max}$ at slightly longer wave lengths than the other, this effect being observable for both the family of bands in the 220 mμ and in the 260 to 275 mμ region. This type of an effect has been the subject of comments by others[7] and seems related to the proximity of the benzene rings in the smaller of the two models.

The spectra of the cycles are somewhat abnormal in the sense that the family of bands in both the lower and higher wave length regions move toward longer wave lengths as compared to the open chain models. This effect intensifies in a regular fashion as the cycles become progressively smaller until in [1.7]paracyclophane, $\Delta\lambda_{\max}$ in the region of lower wave length equals 26 mμ, and in the higher region, 8 mμ. Clearly, as the two rings are brought closer and closer together, these spectral changes become more visible. As with the other smaller paracyclophanes,[2e] two effects are probably responsible for these spectral modifications, one being a transannular electronic coupling of the two chromophores, the other being associated with modification of the benzenoid resonance due to the bending of the two benzene rings into shallow tubs. Of these, the first is probably the more important, since in the passage from the larger to the smaller cycles, the spectral trends observed in passing from the *p,p'*-dialkyl-1,6-diphenylhexane to the *p,p'*-dialkyldiphenylmethane persist and become accentuated. Since the benzene rings of both models are planar, these spectral trends found first in the models and continued in the cycles would seem not to be mainly associated with deviation of the aromatic nuclei of the smaller cycles from a planar geometry.

The variation in distances between the benzene rings in the cycles as the length of the longer bridge is varied cannot be calculated without knowing which bond angles accommodate the strain inherent in the lower homologs. However, some insight can be gained regarding the magnitude of the strain in these molecules by determining their geometry assuming that, (1) the benzene rings are planar and (2) the strain is all concentrated in the phenyl–methylene–phenyl bond

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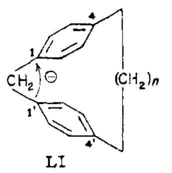
(7) (a) R. C. Cookson and N. S. Wariyar, *J. Chem. Soc.*, 2302 (1956); (b) P. D. Bartlett and E. S. Lewis, THIS JOURNAL, **72**, 1005 (1950); (c) the articles quoted in these references.

angle. Professor D. H. R. Barton was kind enough to make measurements of the distances between the benzene rings utilizing his metal scale models designed for this purpose. Table II records these distances as well as the values for θ in these idealized models.

TABLE II



LI

n	θ	Distance in Å.[a]	
		C-1 to C-1′	C-4 to C-4′
Model[b]	109°	2.50	7.04
6	59	1.51	4.24
7	71	1.78	5.01
8	84	2.06	5.79
9	98	2.32	6.52
10	113	2.57	7.21
11	132	2.81	7.89
12	146	2.92	8.25

[a] Distances measured in models in which benzene rings are planar and all strain is concentrated in bond angle θ. [b] Diphenylmethane.

The shortest methylene chain in LI which can accommodate θ = 109° is one in which n = 10. The rather small differences in ultraviolet spectra between the model and [1.10]paracyclophane are probably associated with the small vibrational and rotational constrictions placed upon the cycle as compared to the open-chain systems. In each case these constrictions would tend to decrease the distances between the rings and increase the population of molecules in which the π-orbitals of C-1 and C-1′ were pointed toward one another. Not until n = 12 do the cycles become large enough to fully free the benzene rings from such constraints.

The infrared spectra of these paracyclophanes vary somewhat with ring size. At 1600 cm.$^{-1}$ a weak band appears in [1.n]paracyclophane with n = 12, and this band becomes increasingly stronger as n becomes smaller until, with n = 7, the absorption is moderately intense. A band appears at 1266 cm.$^{-1}$ in the cycle with n = 9, and becomes more intense as n becomes smaller. This band is absent in the cycles with $n > 9$. In the region from 1200 to 700 cm.$^{-1}$, the smaller rings possess much better defined bands than the larger rings and the open chain compound. All of the compounds have bands in the neighborhood of 1100 cm.$^{-1}$ as follows: with n = 7, 1110 cm.$^{-1}$ (m); n = 8, 1121 and 1100 cm.$^{-1}$ (mw); n = 9, 1113 and 1072 cm.$^{-1}$ (mw); n = 10, 1105 cm.$^{-1}$ (m and unsymmetrical); n = 11, 1114 cm.$^{-1}$ (m); n = 12, 1106 (m); open chain model, 1110 and 1094 (s and non-resolved). A similar situation is found in the 650 to 800 cm.$^{-1}$ region, the bands being as follows: with n = 7, 802 cm.$^{-1}$ (s), 745 cm.$^{-1}$ (ms); 715 and 697 cm.$^{-1}$ (w); n = 8, 792 cm.$^{-1}$ (s), 760 and 725 cm.$^{-1}$ (m); n = 9, 794–785 cm.$^{-1}$ (s and unresolved), 750–755 cm.$^{-1}$ (ms and unresolved), 712 cm.$^{-1}$ (m); n = 10, 805 and 790 cm.$^{-1}$ (m, doublet), 760–755 cm.$^{-1}$ (ms and unresolved), 714 cm.$^{-1}$ (w); n = 11, 791 cm.$^{-1}$ (s), 750–740 cm.$^{-1}$ (m and unresolved); n = 12, 790–780 cm.$^{-1}$ (s and unresolved), 741 cm.$^{-1}$ (m); open chain model, 786 cm.$^{-1}$ (s), 750 cm.$^{-1}$ (m), 694 cm.$^{-1}$ (w).[8] The larger the rings become, the greater becomes the similarity in spectra between the cycles and the open chain models. The strain inherent in the smaller cycles probably places certain restrictions on the stretching and bending vibrations of the various linkages which are absent in the larger rings and the open chain model. In the smaller rings, the aromatic nuclei might be somewhat warped and the molecules relatively rigid and homogeneous in a conformational sense. These features undoubtedly play a role in modifying the spectra of the lower cycles.

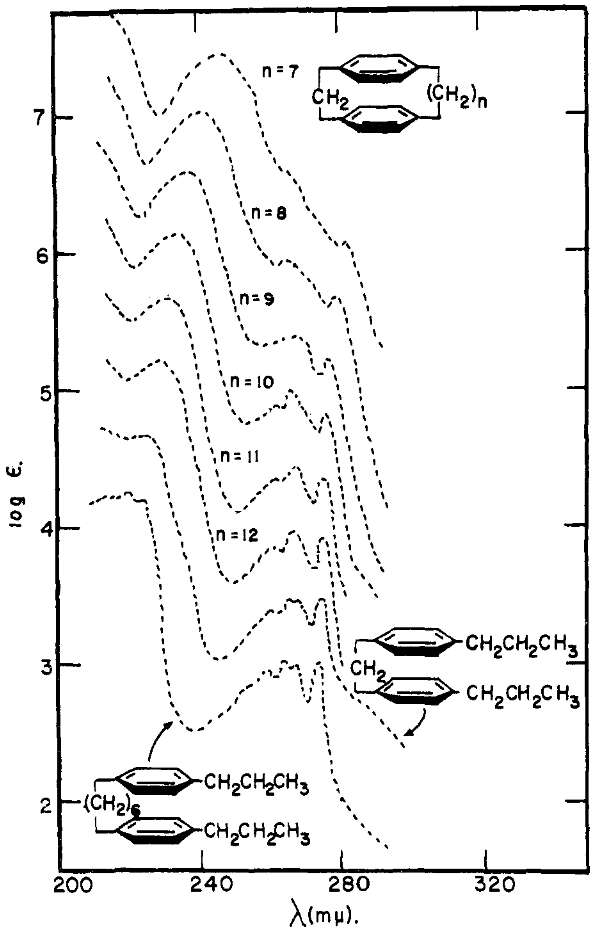


Fig. 1.—Ultraviolet absorption spectra of paracyclophanes and model open-chain compounds in 95% ethanol, Cary recording spectrophotometer, model 11 PMS. All curves except the lowest are displaced upward by 0.5 unit from the curve immediately below.

Experimental[9]

Procedure A: Methyl-4-glutaryldiphenylmethane (VI).—A mixture of 92 g. (0.55 mole) of diphenylmethane, 94 g. (0.57 mole) of γ-carbomethoxybutyryl chloride[10] and 600 ml. of tetrachloroethane was cooled to −7° in an ice–salt-bath. Aluminum chloride (167 g., 1.25 moles) was added to the stirred mixture in small portions over a period of 90 minutes, and the resulting mixture was kept below 0° for 4 hours. This material was allowed to warm to 25°, the dark yellow oil was poured over ice, and the resulting layers were separated. The aqueous solution was extracted with

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[8] s = strong, m = medium and w = weakly absorbing bands.

[9] All melting points are corrected unless otherwise stated; boiling points are uncorrected. Typical examples of each procedure are recorded here.

[10] "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1956, p. 169.

ether, and the extract was added to the organic layer. The combined material was washed with 2 *N* hydrochloric acid, water, dilute sodium bicarbonate solution and again with water. The solution was dried over magnesium sulfate, evaporated, and the residual yellow oil was distilled at 1 mm. The fraction boiling at 210–211° was collected to give 130 g. (80%) of pale yellow material which solidified before the index of refraction could be taken, m.p. 39.5–42°. A small sample was recrystallized twice from petroleum ether to yield white plates (VI), m.p. 41–42°.

Procedure C: **4-(δ-Carboxybutyl)-diphenylmethane (XII).**—The keto esters were reduced by modified Wolff–Kishner reduction,[11] the following procedure being illustrative. A mixture of 129 g. (0.435 mole) of keto ester VI, 56 g. (0.95 mole) of 85% hydrazine hydrate, 89 g. (1.6 moles) of potassium hydroxide and 400 ml. of diethylene glycol was held at reflux for 3 hours. The distillate was then allowed to escape until the pot temperature rose to 205°, the mixture being held at reflux at this temperature for 10 hours. The mixture was then cooled and a liter of water was added. The solution was filtered, cooled to 0° and 150 ml. of concentrated hydrochloric acid was added with vigorous stirring. The white precipitate that separated was allowed to stand for 20 hours at 0° and then collected and allowed to partially dry under a rubber dam. This solid was further dried for 10 hours at 56° at 25 mm. of pressure to give 113 g. (96%) of virtually white acid (XII), m.p. 68–71.5°. A small sample (0.5 g.) was recrystallized twice from petroleum ether to give 0.4 g. (80%) of white needles, m.p. 70–71.2°.

Procedure D: **4-(δ-Carbethoxybutyl)-diphenylmethane (XV).**—A mixture of acid XII (112 g. or 0.42 mole), 140 ml. of absolute ethanol and 7 ml. of concentrated sulfuric acid was held at reflux for 6 hours. The resulting solution was poured over an ice–water mixture and extracted with ether. The ether solution was washed with water, dilute sodium bicarbonate solution and again with water. The solution was dried over magnesium sulfate, the ether evaporated and the remaining yellow oil was distilled. The fraction boiling at 200–202° (1.7 mm.) was collected to give 115 g. (92%), n^{25}D 1.5368, of ester XV.

Procedure E: ***p*-(4-Carbethoxybutyl)-*p*′-(1-keto-3-carbomethoxypropyl)-diphenylmethane (XVIII).**—A mixture of 112 g. (0.38 mole) of ester XV, 58 g. (0.39 mole) of β-carbomethoxypropionyl chloride[9] and 600 ml. of tetrachloroethane was cooled to −7° in an ice–salt-bath. Aluminum chloride (170 g., 1.27 moles) was added in small portions over a period of 105 minutes to the stirred mixture, and the temperature was maintained below 0° for 4 hours. The Friedel–Crafts reaction product was decomposed and the ketone isolated as in procedure A to give 140 g. (90%) of a brown oil which was reduced by the Wolff–Kishner method (see procedure C) without purification. A 3-g. sample of this oil was distilled at a pot temperature of 290–300° and a pressure of 1 mm. to give 2.2 g. (73%) of a pale yellow oil which solidified upon cooling, m.p. 38–41°. This solid was recrystallized twice from benzene–hexane and twice from ether to give white needles (XVIII), m.p. 40–41.5°.

Procedure F: ***p*-(4-Carboxybutyl)-*p*′-(3-carboxypropyl)-diphenylmethane (XXIII).**—Crude ketoester XVIII, 135 g., was added to a mixture of 78.5 g. (1.4 moles) of potassium hydroxide, 42 g. (0.84 mole) of 85% hydrazine hydrate and 400 ml. of diethylene glycol. This mixture was subjected to the conditions of the Wolff–Kishner reaction as described in procedure C to give upon final acidification, 113 g. (86%) of crude diacid XXIII, m.p. 141.5–145.5°. A small sample was recrystallized twice from acetone to give white crystals, m.p. 143.5–146°.

Procedure H: ***p*(4-Carbomethoxybutyl)-*p*′-(3-carbomethoxypropyl)-diphenylmethane (XXIX).**—A mixture of 110 g. of crude diacid XXIII, 500 g. of absolute methanol and 25 ml. of concentrated sulfuric acid was held at reflux for 8 hours. The mixture was poured over ice and extracted with ether. The ether extract was washed with water, dilute sodium bicarbonate and again with water. The solution was dried in the usual manner and the ester was distilled under reduced pressure. The residual dark yellow oil was distilled under high vacuum and the fraction boiling at 250–252° (0.7 mm.) was collected to give 106 g. (89.5%) of a pale yellow oil, n^{25}D 1.5329. A small sample (2 g.) was redistilled at 248–250° (0.5 mm.) to yield 1.5 g. (75%) of a virtually colorless oil (XXIX), n^{25}D 1.5332.

Procedure J: **4-Hydroxy-5-keto[1.9]paracyclophane (XXXIV).**—The acyloin reaction was carried out under high dilution conditions using the apparatus previously described.[2a] Dimethyl ester XXIX (50 g. or 0.130 mole) in 950 ml. of pure xylene was added to 14 g. (0.60 mole) of clean molten sodium in 2 l. of xylene during 50 hours. The mixture was stirred and heated for an additional 0.5 hour, cooled to 0°, and 40 g. (0.67 mole) of acetic acid was slowly added. The polymer and sodium acetate that separated were collected, the xylene was distilled from the filtrates under a steady stream of dry nitrogen, and the residual yellow oil was distilled under high vacuum to give 29.5 g. (70%) of crude acyloin. A sample of this material (10 g.) was distilled at 1 mm. pressure and a pot temperature of 255–270° to give 5.5 g. (55%) of a pale yellow solid, m.p. 93–97.5°. This material was recrystallized twice from hexane and twice from methanol to give white plates of XXXIV, m.p. 96.5–98.3°.

Procedure K: **[1.9]Paracyclophane (XXXIX).**—Zinc, 60 g. or 0.92 mole, was amalgamated with 1.84 g. of mercuric chloride, 185 ml. of water and 1.25 ml. of concentrated hydrochloric acid. A mixture of 6.44 g. (0.02 mole) of ketol XXXIV, 185 ml. of glacial acetic acid and 185 ml. of concentrated hydrochloric acid was added, and the resulting mixture was held at reflux for 45 hours, during which time four 30-ml. portions of concentrated hydrochloric acid were added. The reaction mixture was then cooled, diluted with water and extracted with pentane. The pentane extract was washed with water, dilute sodium bicarbonate solution and again with water. The solution was dried over magnesium sulfate, and the solvent was evaporated to give 5.6 g. (87%) of a pale yellow oil. The residual oil was catalytically hydrogenated in a mixture containing 50 ml. of ethyl acetate and 0.22 g. of platinum oxide. An estimated amount of hydrogen (0.0048 mole) was consumed, a fact indicating the presence of approximately 25% olefin in the product of the Clemmensen reduction. The resulting mixture was filtered, the filtrate was evaporated under reduced pressure, and the colorless oil that remained was crystallized at room temperature to give 5.4 g. (83%) of white plates, m.p. 80–84.5°. A small sample was recrystallized 3 times from methanol to give 80% yield of white plates (XXXIX), m.p. 85.2–86°.

Procedure B: **Dimethyl-bis-(4-glutarylphenyl)-methane (IX).**—A mixture of 65.5 g. (0.39 mole) of diphenylmethane, 130 g. (0.79 mole) of γ-carbomethoxybutyryl chloride[10] and 600 ml. of tetrachloroethane was cooled to −5° in an ice–salt-bath. Aluminum chloride (225 g., 1.7 moles) was added to the stirred mixture in small portions over a period of 110 minutes, and the resulting mixture was kept below 0° for 4 hours. This material was allowed to warm to 25°, the dark yellow oil was poured over ice, and the organic layer was separated from the water layer. The water layer was then extracted with ether, and the ether extract was added to the tetrachloroethane layer. The combined extracts were washed with 2 *N* hydrochloric acid, water, dilute sodium bicarbonate solution and again with water. The solution was dried over magnesium sulfate, and the solvent was evaporated under reduced pressure. The residual dark yellow oil solidified upon cooling to give 116 g. (71%) of virtually colorless plates, m.p. 96–99°. A small sample was recrystallized four times from a mixture of benzene and hexane to give an 80% yield of white plates of IX, m.p. 97.5–99.2°.

Procedure G: **Bis-[4-(δ-carboxybutyl)-phenyl]-methane (XXIV).**—Crude ketonic ester IX (see above), 115 g. or 0.27 mole, was added to a mixture of 46 g. (0.78 mole) of 85% hydrazine hydrate, 112 g. (2 moles) of potassium hydroxide in 400 ml. of diethylene glycol. This mixture was subjected to the conditions of the Wolff–Kishner method as described in procedure C to give upon final acidification 96 g. (96%) of a crude material, m.p. 135–139°. A small sample was recrystallized four times from ether to give an 80% yield of a white solid (XXIV), m.p. 138.5–140°.

Procedure L: **4-(β-Carbethoxyethyl)-diphenylmethane (XIV).**—A mixture of 155 g. (0.69 mole) of 4-propionyldiphenylmethane (prepared by procedure A), 28 g. (0.87 mole) of sulfur and 304 g. (3.5 moles) of morpholine was subjected to the conditions of the Willgerodt reaction.[12] The mixture was held at reflux for 36 hours, poured into

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[11] Huang Minlon, THIS JOURNAL, **68**, 2487 (1946).

[12] (a) E. Schwenk and E. Bloch, *ibid.*, **64**, 3051 (1942); (b) J. Abell and D. J. Cram, *ibid.*, **76**, 4406 (1954).

water, and the resulting suspension was extracted with chloroform. The dark extract was washed with water, dried, filtered and the solvent was evaporated to leave a residue of 235 g. of a dark red oil. The crude thiomorpholide was hydrolyzed by refluxing it with a mixture of 118 g. (2.1 moles) of potassium hydroxide, 120 ml. of water and 440 ml. of 95% ethanol for 36 hours. The reaction mixture was diluted with water, acidified with concentrated hydrochloric acid and the light brown solid that separated was collected and partially dried under a rubber dam. This solid was further dried at 56° and 25 mm. of pressure to a constant weight, 150 g. (89%) of crude acid XI. This acid was converted without purification to its ethyl ester (procedure D).

Procedure M: 4-(β-Carbomethoxyethyl)-4'-(γ-carbomethoxypropyl)-dicyclohexylmethane (XLVII).—Diester XXVII (109 g. or 0.31 mole) prepared by a sequence involving XI → XIV → XVII → XXI → XXVII was dissolved in 150 ml. of glacial acetic acid, and 2.0 g. of platinum oxide was added to the solution. The mixture was hydrogenated catalytically under pressure at room temperature until the theoretical amount of hydrogen was absorbed, filtered and the solvent was distilled from the filtrate at reduced pressure. The yellow residue was distilled under high vacuum, and the fraction boiling at 214–215° (1 mm.) was collected to yield 100 g. (89%) of virtually colorless oil (XLVI), $n^{25}\text{D}$ 1.4817. Although this oil was undoubtedly a mixture of diastereomers, they were not separated, and the mixture was submitted directly to procedure J.

Perhydro[1.7]paracyclophane (XLIX).—Acyloin XLVIII was prepared from 61.4 g. of diester XLVII by procedure J to give a mixture of materials, which was separated into the following fractions by distillation: (1) b.p. 180–215° (~ 1 mm.), 12.14 g., $n^{25}\text{D}$ 1.4760; (2) b.p. 215–218° (~ 1 mm.), 14.52 g., $n^{25}\text{D}$ 1.4750; (3) b.p. 219–220°, 30.86 g., $n^{25}\text{D}$ 1.4723. Fractions 2 and 3 were combined and submitted to procedure K, 1.2 g. of distilled colorless oil (bath temperature 245°, 1 mm. pressure) being the product. This material was treated with 0.35 g. (0.0082 mole) of lithium aluminum hydride in anhydrous ether for two hours, and the product was isolated in the usual way as a pale yellow oil. This material was chromatographed on 100 g. of neutral alumina (activity 1)[13] with pentane as the developer. The product (XLIX) was eluted with pentane, weight 0.94 g., m.p. 78–80°. This material was recrystallized from a methanol–ethanol mixture to give 0.85 g. of white needles of XLIX, m.p. 78.4–80°.

Procedure N: [1.7]Paracyclophane (L).—The impure saturated hydrocarbon, XLIX (1.5 g. of oil) was heated in a micro Kjeldahl flask with 0.19 g. of 10% palladium-on-charcoal. Only 69% of the theoretical amount of hydrogen was evolved during 4 hours as the temperature was gradually raised from 250° to 320°. The crude product was dissolved in pentane, the solution was filtered and the solvent was evaporated in vacuum. The residual oil was distilled under high vacuum to give 1.0 g. of a colorless liquid, bath temperature 207° (1 mm.), $n^{25}\text{D}$ 1.5398. This liquid was absorbed on 500 g. of very active neutral alumina and eluted with pentane. A total of 129 50-ml. fractions of the eluate was collected and, on the basis of similarities in their ultraviolet absorption spectra, were combined in the following way to give 5 combined fractions: fraction A, flasks 1–13, contained 110 mg.; fraction B, flasks 14–35, contained 105 mg.; fraction C, flasks 36–83, contained 360 mg.; fraction D, flasks 84–121, contained 325 mg.; fraction E, flasks 122–129, contained 50 mg. The ultraviolet absorption spectrum of fraction C appeared to be the most like that expected for the desired cycle (L), and it was rechromatographed on 200 g. of very active alumina. The middle fractions of the eluate were combined, and the product was crystallized from methanol to give 0.032 g. (2%) of L, m.p. 76.5–77.2° (hard white needles).

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

LOS ANGELES 24, CALIFORNIA

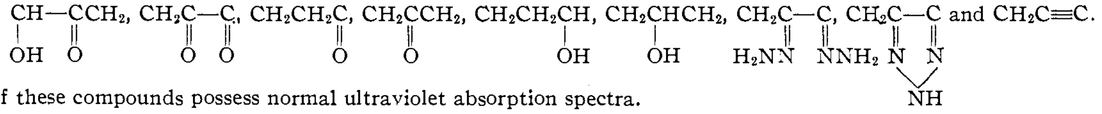
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Macro Rings. XVI. The Synthesis and Side Chain Chemistry of [9]Paracyclophane[1]

BY DONALD J. CRAM AND M. FARID ANTAR

RECEIVED JANUARY 14, 1958

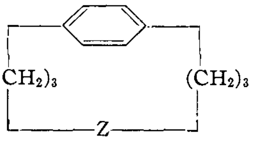
The synthesis and properties of a number of [9]paracyclophanes carrying functional groups in the methylene belt are described. These compounds possess the general structure I and Z represents the functions:



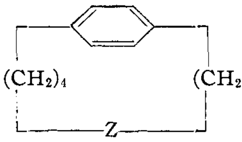
$$\underset{\displaystyle OH}{\underset{|}{CH}}-\underset{\displaystyle O}{\underset{\|}{C}}CH_2,\ CH_2\underset{\displaystyle O}{\underset{\|}{C}}-\underset{\displaystyle O}{\underset{\|}{C}},\ CH_2CH_2\underset{\displaystyle O}{\underset{\|}{C}},\ CH_2\underset{\displaystyle O}{\underset{\|}{C}}CH_2,\ CH_2CH_2\underset{\displaystyle OH}{\underset{|}{CH}},\ CH_2\underset{\displaystyle OH}{\underset{|}{CH}}CH_2,\ CH_2\underset{\displaystyle H_2NN}{\underset{\|}{C}}-\underset{\displaystyle NNH_2}{\underset{\|}{C}},\ CH_2\underset{\underset{\displaystyle NH}{\diagdown\;\diagup}}{\underset{N\quad N}{\underset{\|\quad\|}{C-C}}}\text{ and }CH_2C{\equiv}C.$$

All of these compounds possess normal ultraviolet absorption spectra.

In papers V[2a] and XI[2b] of this series are described the preparation and reactions of compounds based on the [10]paracyclophane parent structure, of

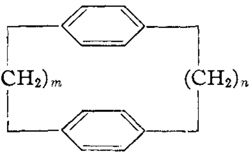


I

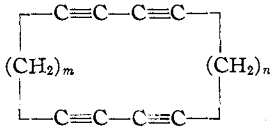


$$\begin{array}{l}\text{II, } Z = CH{=}CH_2\\ \qquad\quad\ \ \|\\ \qquad\quad\ \ O\\ \text{III, } Z = C{\equiv}CCH_2\end{array}$$

which II and III are representative compounds. Other investigations of paracyclophanes[3] such as IV established that if the two aromatic rings are closer than 3.4 Å. apart (normal van der Waals distance), abnormal ultraviolet spectra result. With $m = n$



IV



V

$= 4$, the spectrum is normal, but abnormal when $m = 3$, $n = 4$, since in the latter compound the benzene rings are pressed to within 2.84 Å. at their points of attachment to the smaller methylene bridge.[3] That such effects are not limited to this particular type of structure is shown by the unusual spectrum of II as compared to open chain

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[1] This work was supported generously by a grant from the National Science Foundation.

[2] (a) D. J. Cram and H. U. Daeniker, THIS JOURNAL, **76**, 2743 (1954); (b) D. J. Cram and M. Cordon, *ibid.*, **77**, 4090 (1955).

[3] D. J. Cram, N. L. Allinger and H. Steinberg, *ibid.*, **76**, 6132 (1954).