this system they traveled equal distances. Angyal[11] further found identical R_f values in four other solvent systems. Dr. A. B. Foster tested a sample of the synthetic ether in his borate ionophoresis system,[7] and found that the compound paralleled natural bornesitol in its behavior.

MADISON, WISCONSIN

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

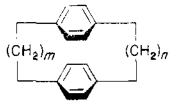
Macro Rings. VII. The Spectral Consequences of Bringing Two Benzene Rings Face to Face[1]

BY DONALD J. CRAM, NORMAN L. ALLINGER[2] AND H. STEINBERG

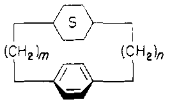
RECEIVED MAY 12, 1954

The preparation of the paracyclophane with $n = m = 3$, of II with $n = 3$, $m = 4$ and with $n = m = 4$, and of III with $n = 12$ are reported. The variations in spectral properties of these classes of compounds with their molecular geometries are discussed. The ultraviolet absorption spectra of *cis*- and *trans*-1,2-diphenylcyclopentane are compared.

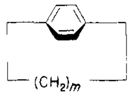
The previous papers in this series[3] have reported the preparation of the series of eight paracyclophanes I in which $n = m$ and in which $n = m - 1$ for all values of n and m from $n = m = 2$ to $n = m = 6$, with exception of the compound in which $n = m = 3$. The less symmetrical cycles (I) with $n = 2, m = 4$, with $n = 3$ and $m = 6$, and with $n = 4$, $m = 6$ have also been reported,[3] as well as compounds of class III with $m = 9$[4a] and 10.[3e,4b]



I

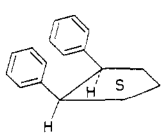


II



III

These two groups of compounds (I and III) offer unique opportunities for the study of certain kinds of transannular electronic and steric effects on physical and chemical properties. Spectral abnormalities, particularly in the ultraviolet region, have been observed to characterize the smaller paracyclophanes I,[3a] and have been attributed to one or both of the following causes: (1) π-electron interactions between the two benzene rings, (2) distortion of the benzene rings from their normal planar configurations. The present investigation reports an attempt to separate and identify these effects through a comparison of the spectral properties of three types of compounds: the paracyclophanes (I) themselves; compounds belonging to classes II and III; compounds possessing the geometry of IV.



IV

In compounds of class I, although the smallest obtainable member ($n = m = 2$)[5a] contains nonplanar benzene rings,[5] the possibility is evident that as the steric constraints are released by increasing the length of the methylene bridges the aromatic nuclei might become planar before the π-electrons of each ring cease to affect each other's spectral characteristics. In compounds of class II and III the possibility exists that bent benzene rings might be produced without the complicating feature of a second aromatic nucleus being in the vicinity of the first. Finally, in compounds of class IV, it was hoped that two benzene rings could be brought face to face without any accompanying complications due to distortion of the aromatic rings from planar configurations.

Results

The synthesis of the paracyclophane with $m = n = 3$ was carried out by the sequence formulated. The mixture of the four *cis–trans* isomers of diester IX obtained by the reduction of the aromatic diester VIII was not separated into its components, but was used directly in the acyloin condensation. The impure acyloin (probably a mixture of position isomers) was submitted directly to a modified Clemmensen reduction, the saturated hydrocarbon XI being obtained in a 1% over-all yield from diester IX. This yield is indicative of the unfavorable steric situation found for the ring-closing step and compares with the yields for analogous sequences in the preparation of the two next larger cycles as follows: compound I with $m = 3$, $n = 4$, yield 6%; I with $m = n = 4$, yield 22%. Dehydrogenation of the saturated hydrocarbon furnished the aromatic cycle, XII.

Several other potential syntheses of XII were also investigated. Reduction of unsymmetrical diester VIII with lithium aluminum hydride followed by treatment of the resulting diol with hydrogen bromide furnished the dibromide XIII. This substance failed to cyclize when subjected to the conditions of the Wurtz reaction, as had the dibromide XIV previously.[3d] Similarly, an attempt to obtain XII by an intermolecular Wurtz reaction of dibromide XV and p-dibromobenzene failed to give the desired cycle. It would appear that the successful application of the Wurtz reaction to preparation of the paracyclophanes is limited to those com-

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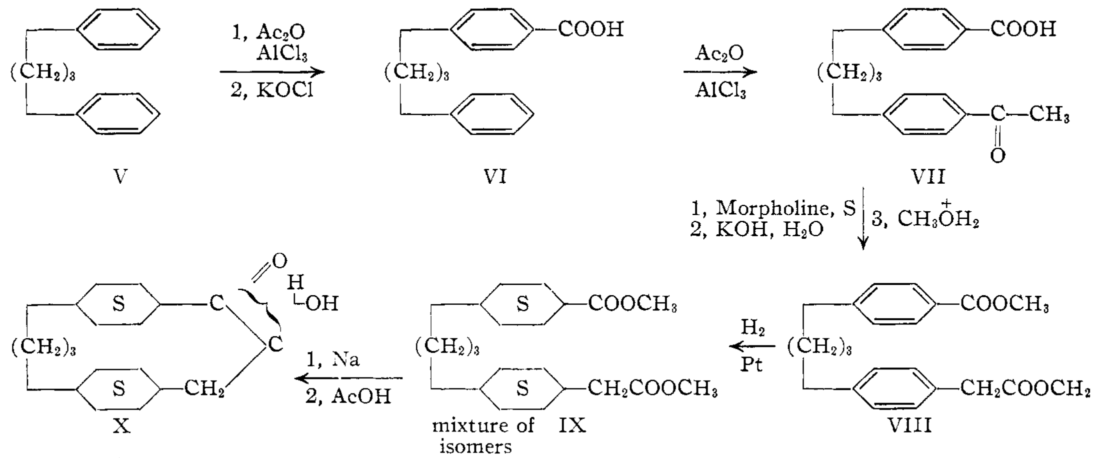
[1] This work was supported in part by the Office of Naval Research.

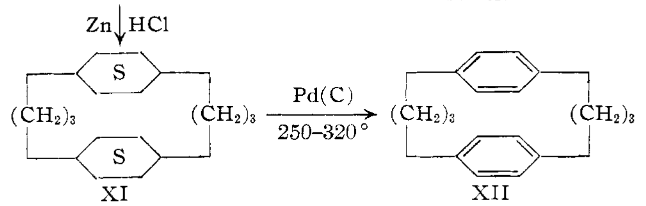
[2] Dow Predoctoral Fellow at U.C.L.A., 1953–1954.

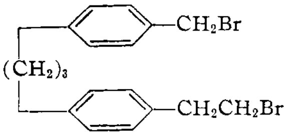
[3] (a) D. J. Cram and H. Steinberg, THIS JOURNAL, **73**, 5691 (1951); (b) H. Steinberg and D. J. Cram, *ibid.*, **74**, 5388 (1952); (c) D. J. Cram and N. L. Allinger, *ibid.*, **76**, 726 (1954); (d) N. L. Allinger and D. J. Cram, *ibid.*, **76**, 2362 (1954); (e) D. J. Cram and H. U. Daeniker, *ibid.*, **76**, 2743 (1954); (f) J. Abell and D. J. Cram, *ibid.*, **76**, 4406 (1954).

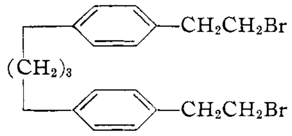
[4] (a) M. F. Bartlett, S. K. Figdor and K. Wiesner, *Canadian J. Chem.*, **30**, 291 (1952); (b) K. Wiesner, D. M. MacDonald, R. B. Ingraham and R. B. Kelly, *Canadian J. Research*, **B28**, 561 (1950).

[5] (a) C. J. Brown, *J. Chem. Soc.*, 3265 (1953); (b) 3279 (1953).

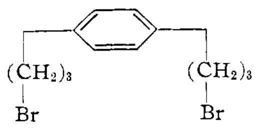


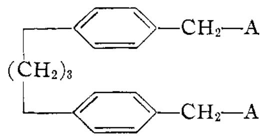


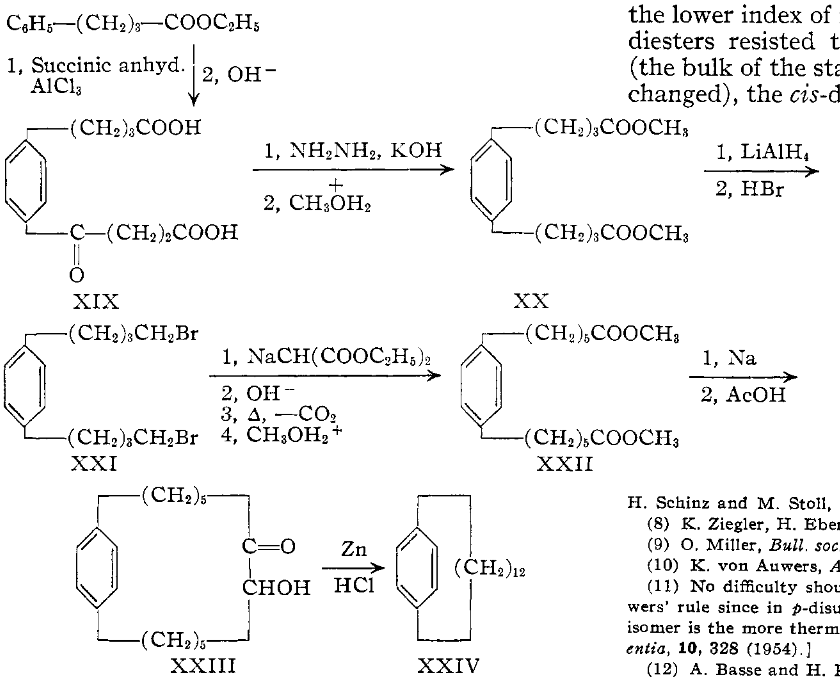

XIII


XIV

pounds typified by XVI in which both bromide functions are of the benzyl type.[3a]


XV


XVI, A = Br
XVII, A = COOH
XVIII, A = CN



Other approaches to the synthesis of cycle XII were equally discouraging. The pyrolysis of XVII[3d] either as the free diacid[6] or as the thorium salt[7] gave no isolable cyclic product. The nitrile XVIII under the conditions of a Ziegler cyclization[8] also failed to yield the desired material, as did the dibromide XVI in an attempted dialkylation of malonic ester.

The synthesis of the cycle, *p*-dodecamethylenebenzene (XXIV), is outlined in the formulation. Numerous attempts were made to ring-close diester XX through the acyloin reaction, but only starting material and small amounts of polymer were obtained. In a further attempt to obtain III (m = 8), the aromatic ring of diester XX was reduced to the corresponding cyclohexane derivative XXV, both isomers being isolated, one in a pure state, the other slightly contaminated with its isomer. The isomer obtained as the minor component was assigned the *trans* structure by analogy with the results obtained in the reduction of *p*-xylene.[9] This provisional assignment is in accord with von Auwers' rule[10] that *trans* isomers of this type possess the lower index of refraction.[11] Since both of these diesters resisted the acyloin ring-closure reaction (the bulk of the starting material was recovered unchanged), the *cis*-diester XXV was converted to the corresponding acid chloride XXVI. The acyloin reaction has been carried out successfully on acid chlorides in simple cases,[12] but not in cyclization reactions. When applied to the diacid chloride XXVI, the acyloin reaction produced polymer, no starting material being recovered. An attempt to prepare cycle III with m = 8 by a ring-closing Wurtz reac-

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[6] M. Szwarc, *J. Chem. Phys.*, **16**, 128 (1948).

[7] L. Ruzicka, W. Brugger, M. Pfeiffer, H. Schinz and M. Stoll, *Helv. Chim. Acta*, **9**, 499 (1926).

[8] K. Ziegler, H. Eberle and H. Ohlinger, *Ann.*, **504**, 94 (1933).

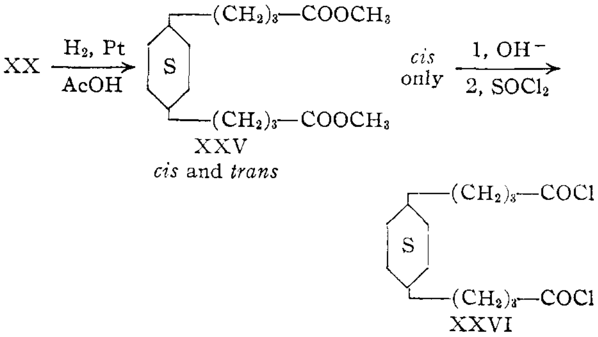
[9] O. Miller, *Bull. soc. chim. Belg.*, **44**, 513 (1935).

[10] K. von Auwers, *Ann.*, **420**, 84 (1920).

[11] No difficulty should be experienced here in applying von Auwers' rule since in *p*-disubstituted cyclohexane derivatives, the *trans* isomer is the more thermodynamically stable [N. L. Allinger, *Experientia*, **10**, 328 (1954).]

[12] A. Basse and H. Klinger, *Ber.*, **31**, 1217 (1898).

tion with dibromide XXI as starting material also failed.



The two half-reduced paracyclophanes (II) with $m = 3, n = 4$ and $m = n = 4$ were prepared by the hydrogenation (glacial acetic acid with a platinum catalyst) of one of the two benzene rings of I with $m = 3, n = 4$ and $m = n = 4$, respectively.

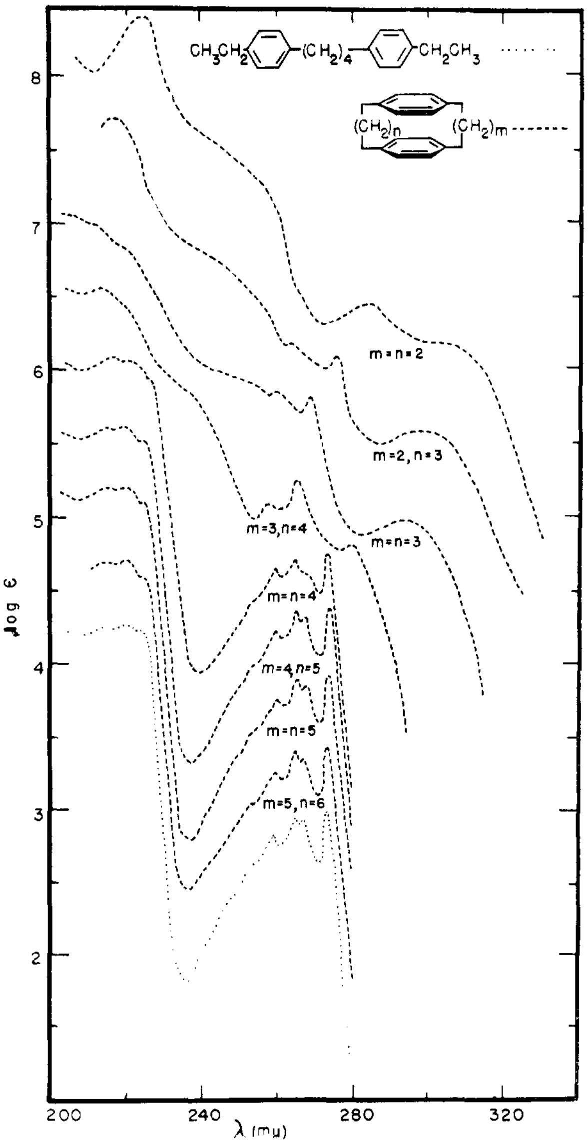


Fig. 1.—Ultraviolet absorption spectra of the more symmetrical paracyclophanes in 95% ethanol (Cary spectrophotometer, model PMS). The curves, with the exception of the open-chain model at the bottom, have been displaced upward on the ordinate axis by 0.5 log ε unit increments from the curve immediately below.

Discussion

Figure 1 records the ultraviolet absorption spectra of the paracyclophanes I in which n and m are varied stepwise one carbon at a time from $m = n = 2$ to $m = 5$, $n = 6$. The most striking feature characterizing the relationships between these spectra is the discontinuity in the progression of the curves from normal (as compared to open-chain models) to abnormal as the values of m and n become small. Thus I with $m = n = 4$ differs only slightly in its spectral properties from I with $m = n = 5$ but differs markedly from I with $m = 3$, $n = 4$. This discontinuity is apparent in both the region of high intensity ($\lambda \sim 215$ mμ) and that of low intensity absorption ($\lambda \sim 270$ mμ), the series of bands in both places moving toward longer wave lengths and lower intensities as the values of m and n become smaller than 4. A similar discontinuity is found in the spectra of the more unsymmetrical paracyclophanes (see Fig. 2) in which $n \leqq m - 2$, again the requirement for a normal spectrum being that both m and n be equal to or greater than 4. As the bands move toward longer wave lengths, they decrease in intensity, and the ϵ's of even the larger cycles ($m \geqq 4$, $n \geqq 4$) are all about 10% below those of the open-chain models.

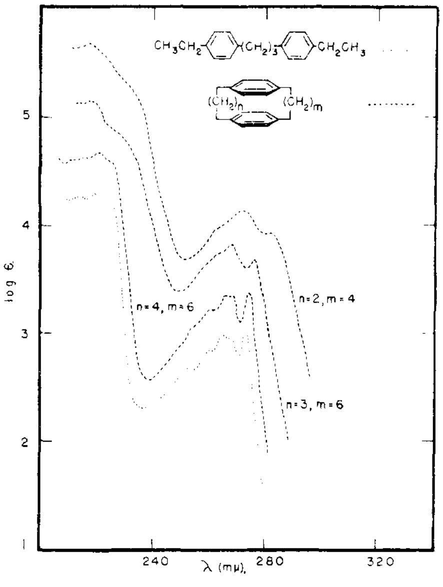
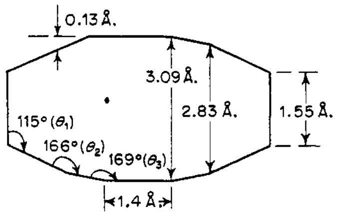


Fig. 2.—Ultraviolet absorption spectra of the relatively unsymmetrical paracyclophanes in 95% ethanol (Cary spectrophotometer, model PMS). The curves, with the exception of the open-chain model at the bottom, have been displaced upward on the ordinate axis by 0.5 log ε unit increments from the curve immediately below.

Distortion of the Aromatic Rings from Planar Configurations.—The establishment of the fact that the aromatic nuclei in the cycle I with $m = n = 2$ are distorted from the normal planar configuration[5] suggests that the same thing might be true of some of the other smaller members of the homologous series. In structure A (the profile of the paracyclophane in which $m = n = 2$)[5] it is evident that strong repulsive forces are acting between the two benzene rings.

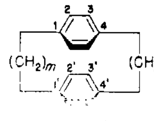


These data fix a *lower limit* of 3.09 Å. for the distance that two benzene rings can be from one another (face to face) without strong repulsive forces coming into play.

Table I reports the results of calculations of the maximum inter-benzoid distances for the paracyclophanes, the assumptions being made that: (a) the aromatic rings are planar; (b) the bond distances are normal and the bond angles are as normal as possible; (c) the two rings are as directly over one another as possible. These calculations indicate that in those cycles with $n = 3$ or less and $m = 4$ or less, the interbenzenoid distances at either one or both ends of the molecule must be *less than* 3.09 Å. The tentative conclusion is evident that the benzene rings are non-planar in the cycles where $m = n = 3$ or smaller, and that other bond angles are distorted, the distortion being greater the smaller the values of m amd n.[13] Furthermore, the cycles with both m and n equal to 4 or *more* are probably planar, the geometry of the compounds having $m = 3$ and $n = 3$ to 6 being ambiguous.

TABLE I

CALCULATED[a] MOLECULAR GEOMETRY (IDEALIZED) OF PARACYCLOPHANES, AND SHIFTS IN ABSORPTION BANDS OF THE ULTRAVIOLET SPECTRA FROM NORMALITY[b]

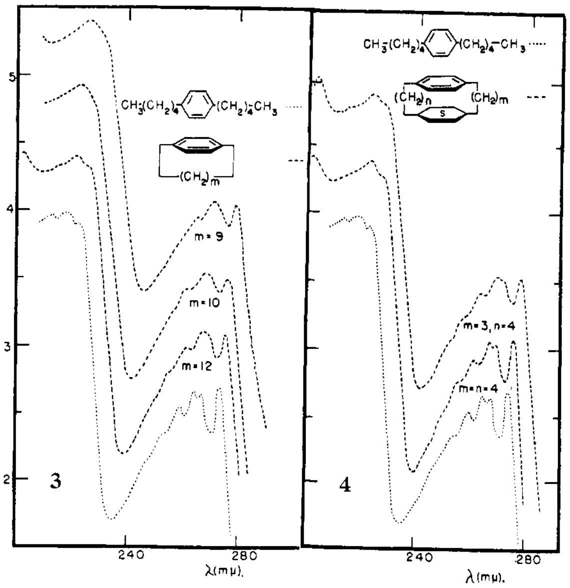


Cmpd.		Dist., Å. C-1	C-4	λ_{max} of cycles − λ_{max} open-chain models Bands at λ_{max} for model, mμ[c]						
m	n	to C-1′	to C-4′	214	219	223	259	265	267	273
2	2	1.54	1.54	..	6	21[d]	..	21	..	29[d]
2	3	1.80	2.26	3	..	20[d]	7	10	..	26
2	4	2.12	3.16	2	7[d]	10[d]	6[d]	6	..	9
3	3	2.52	2.52	−2[d]	−1[d]	23[d]	2	4	..	21
3	4	2.84	3.41	1	0[d]	9[d]	−2	1	..	7
3	6	3.50	5.27	3	..	2[d]	4[d]	3	..	3
4	4	3.73	3.73	3	1	3[d]	1	1	1	1
4	5	..	..	2	1	2	1	1	1	1
4	6[e]	.	..	1	1	2	1	1	1	1

[a] Based on bond distances and where possible on bond angles taken from ref. 14. [b] The spectra of the bis-(*p*-alkylphenyl)-alkanes appear to be identical to one another.[3a] [c] Model is bis-(*p*-ethylphenyl)-butane. [d] Shoulders (estimated). [e] Spectra of larger paracyclophanes are identical with I, $m = 4$, $n = 6$.

Crystallographic data on a number of aromatic compounds in which the aromatic nuclei occupy parallel planes indicate an interplanar distance of approximately 3.40 Å. for quite a variety of substances.[14] Thus graphite,[15a] copper tropolone,[15b] phthalocyanine,[15c] nickel phthalocyanine[15d] and coronene[15e] all possess crystallographic organizations of this type. The distance of 3.40 Å. between the faces of aromatic nuclei packed in a crystal lattice therefore appears to be normal for those molecules between which only weak van der Waals forces operate. The fact that the ultraviolet absorption spectrum of I with $m = 3$, $n = 4$ is abnormal correlates with the calculated idealized distance between the benzenes being less than 3.40 Å., at least at one end (2.84 Å. at one end and 3.41 Å. at the other). Furthermore, the spectrum of I with $m = n = 4$ is normal, the calculated idealized distance between the aromatic rings being greater than 3.40 Å. (distance of 3.73 Å.).

In an attempt to determine whether the abnormal spectra of the smaller paracyclophanes could be attributed solely to perturbations arising out of the non-planarity of the aromatic rings, compounds of class III were examined with the hope that m could be made small enough to substantially distort the benzene ring from its normal configuration. Figure 3 records the ultraviolet absorption spectra of III with $m = 9$, 10 and 12, along with that of an open-chain model. As m is decreased, trends appear in these spectra that are similar in certain respects to those found in the paracyclophanes as n and m are decreased. Thus, the maxima in both general regions of absorption tend to move toward longer wave lengths and lower intensities, and the fine structure tends to be eliminated. Molecular mod-



Figs. 3 and 4.—Ultraviolet absorption spectra of cycles III (Fig. 3) and II (Fig. 4) in 95% ethanol (Cary recording spectrophotometer, model PMS). The curves, with the exception of the open-chain model compound at the bottom, have been displaced upward on the ordinate axis by 0.5 log ε unit increments from the curve immediately below.

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[13] The geometry of compound I with $m = n = 3$ is being examined through X-ray crystallographic analysis in these laboratories by Dr. K. N. Trueblood.

[14] J. M. Robertson, "Organic Crystals and Molecules," Cornell University Press, Ithaca, N. Y., 1953, pp. 157, 206, 27, 270, 274.

[15] (a) H. Ott, *Ann. Physik*, **85**, 81 (1928); (b) J. M. Robertson, *J. Chem. Soc.*, 1222 (1951); (c) 615 (1935), and 1195 (1936); (d) J. M. Robertson and I. Woodward, *ibid.*, 219 (1937); (e) J. M. Robertson and J. G. White, *ibid.*, 607 (1945).

els of III with $m = 9$ suggest that either the aromatic ring is non-planar, or the bond angles in the methylene bridge are modified, or the two effects combine to relieve the steric repulsions inherent in the system. The fact that III with $m = 8$ could not be made suggests that III with $m = 9$ is at least as strained as the paracyclophanes with $m = n = 3$ or $m = 3$, $n = 4$, since the same kinds of ring-closing reactions on the same kinds of starting materials were utilized.[16]

Similar trends are evident in the ultraviolet spectra (see Fig. 4) of the paracyclophanes in which one benzene ring has been reduced to a cyclohexane ring (II).[17] A cyclohexane is somewhat thicker than a benzene ring, but it is impossible to say which system (I or II with m and n the same) is the most constrained since the bond orientations in II are more adaptable than in I. Judging by the spectra, the benzene rings in II with $m = 3$, $n = 4$ and in III with $m = 10$ are about comparably constrained. The conclusion that can be drawn from these spectral comparisons is that the warping of the aromatic rings in the paracyclophanes is *at least* partially responsible for their abnormal electronic spectral properties.

Transannular Electronic Effects in the Smaller Paracyclophanes.—It was suggested previously[3a] that the abnormal ultraviolet absorption spectra of the smaller paracyclophanes might be due, at least partially, to transannular resonance effects associated with either the ground or excited states of the two aromatic systems. Ingraham[18] carried out both valence bond (V.B.) and molecular orbital (L.C.A.O.) calculations in an attempt to determine whether or not there is any stabilization of the molecule due to $2p\sigma$-type bonds between the two benzene rings of I, $m = n = 2$. Neglecting effects due to the two bridging chains and non-planarity of the benzene rings, the valence bond method predicted 4 kcal. more resonance energy for I ($m = n = 2$) than for two infinitely separated benzene rings. However, 16 kcal. was required to bring two benzene rings face to face and 3 Å. apart from infinite separation) due to repulsive forces. On the other hand, the L.C.A.O. method due to its neglect of repulsive forces predicted the same energy for the two benzene rings face to face as completely separated, unless one or both aromatic rings were deficient one electron. The valence bond calculation also indicated a slight shift of the 260 mμ benzene band toward shorter wave lengths.

In connection with the question of the nature of the electronic forces operating between the two benzene rings in the smaller paracyclophanes, the geometries and spectral properties of a number of molecular complexes are of interest. In most of the complexes that involve aromatic nuclei, one component of the complex carries electron-withdrawing and the other electron-releasing groups, and the forces binding the two components of molecular complexes in general are considered to be polar in character (acid–base interactions in the Lewis sense).[19] In a number of cases the crystal structures of complexes involving two aromatic components have been determined,[20a,e] and frequently the molecules are stacked in columns, with the two components forming alternate layers parallel to each other, the aromatic rings not having coaxial orientation. In these crystals, the distances between the parallel aromatic nuclei vary from 3.2 to 3.5 Å. In *p*-nitroaniline where the nitro group of one ring overlies part of the ring of a second molecule (the rings occupy parallel planes) the line of closest intermolecular O . . . C approach is 2.66 Å., a distance much shorter than that found in ordinary crystals.[20b–d] Some of these molecular complexes persist at least partially in solution[19b,21] and absorb light at longer wave lengths and lower intensities than do the separate components of the complex. Finally, Nakamoto measured the dichroisms of the π-electron absorption bands in the ultraviolet spectra of the crystals of a number of common aromatic compounds,[22a] as well as of the crystals of four molecular complexes of the type discussed above.[22b] In the former case, the light absorbed with its electric vector vibrating *parallel* to the plane of the aromatic nuclei was always of longer wave length (ϵ being higher) than the light with its vector vibrating *perpendicular* to the same plane. In the latter case the situation was reversed. These effects were rationalized[22b] as follows. In the simple crystals the overlap of π-electron clouds in the direction perpendicular to the benzene rings is small (the rings are 3.4–3.5 Å. apart), and accordingly the density distribution of π-electrons is larger and the electrons are more mobile in the direction parallel than in the direction perpendicular to the rings. In the crystals of complex, the overlap of π-electron clouds in the direction perpendicular to the benzene rings is larger (the rings are 3.16–3.26 Å. apart), and thus the density distribution of π-electrons becomes larger and the electrons become more mobile in the direction perpendicular than in the direction parallel to the rings.

The distance between the benzene rings in the smaller paracyclophanes is either smaller or comparable to that found in the above molecular compounds. Furthermore, the general progression of bands in the ultraviolet spectra of the paracyclophanes toward longer wave lengths as the two benzene rings get closer together might possibly be partially associated with transannular resonance effects, the excited states being more resonance stabilized than the ground states, as is common in

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(16) In the preparation of I with $m = n = 3$ and $m = 3$, $n = 4$, the fully reduced *cis*-diester (such as IX) underwent ring closure. In the attempted preparation of III with $m = 8$, the fully reduced *cis*-diester XXV failed to ring close in even trace amounts. Compound III with $m = 9$ was prepared by a sequence similar to that employed for III with $m = 12$. The former synthesis will be reported in a future paper in this series.

(17) Attempts to prepare II with $m = n = 2$ failed.

(18) L. L. Ingraham, *J. Chem. Phys.*, **18**, 988 (1950).

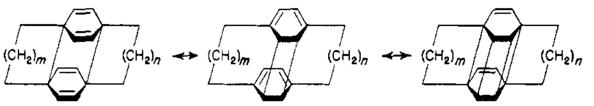
(19) (a) R. S. Mulliken, THIS JOURNAL, **72**, 600 (1950), and **74**, 811 (1952); (b) J. Landauer and H. McConnell, *ibid.*, **74**, 1221 (1952); (c) W. Brackman, *Rec. trav. chim.*, **68**, 147 (1949); M. J. S. Dewar, *J. Chem. Soc.*, 406 (1946); (d) J. Weiss, *ibid.*, 245 (1942).

(20) (a) H. M. Powell, G. Huse and P. W. Cooke, *ibid.*, 153, 435 (1943); (b) S. C. Abrahams and J. M. Robertson, *Acta Cryst.*, **1**, 252 (1948); (c) P. J. A. McKeown, A. R. Ubbelohde and I. Woodward, *ibid.*, **4**, 391 (1951); (d) S. C. Abrahams, THIS JOURNAL, **74**, 2692 (1952); (e) K. Osaki and M. Matsuda, *Acta Cryst.*, in press.

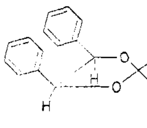
(21) L. Michaelis and S. Granick, THIS JOURNAL, **66**, 1023 (1944).

(22) (a) K. Nakamoto, *ibid.*, **74**, 390, 392 (1952); (b) **74**, 1739 (1952).

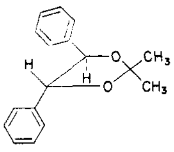
organic molecules. Although repulsive forces between the two rings undoubtedly predominate, the type of structures indicated in B might stabilize the cycles somewhat as has been indicated in the valence bond calculation of Ingraham.[18] If this type of stabilization exists, it would be different from that found in the molecular complexes in two respects: the attractive forces would be far less polar in character; the rings have coaxial orientation.



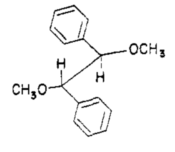
In an attempt to determine the consequences of bringing two benzene rings face to face without the complication of deforming the aromatic rings, the ultraviolet absorption spectra of *cis*- and *trans*-1,2-diphenylcyclopentane[23] were compared, as well as those of XXVII and XXIX (Fig. 5). A very slight trend is evident for the absorption bands to move toward longer wave lengths and lower intensities as one passes from the structures in which the two phenyls are more *trans* (*trans*-1,2-diphenylcyclopentane or compound XXIX) to those in which the two phenyls are more *cis* (*cis*-1,2-diphenylpentane or compound XXVII). Although this trend is qualitatively similar to that observed for the paracyclophanes as m and n become smaller, quantitatively there is no comparison. Furthermore, the differences might be due to other than transannular effects. If the two phenyl groups in *cis*-1,2-diphenylcyclopentane and in XXVII are completely eclipsed, the benzene rings possess a geometry relative to each other comparable to that of the paracyclophane with $m = 2$, $n = 4$. There is considerable doubt, however, that two phenyl groups *cis* to one another on a five-membered ring are eclipsed completely. Aston, *et al.*,[24] concluded from thermal data that cyclopentane was not planar, and Pitzer, *et al.*,[25] calculated from spectral and thermal data that the puckered was more stable than the planar configuration. Donahue and Trueblood[26] have determined the crystal structure of hydroxyproline and found that the carbon carrying the hydroxyl group is 0.4 Å. out of the plane of the other four-ring atoms.



XXVII



XXVIII



XXIX

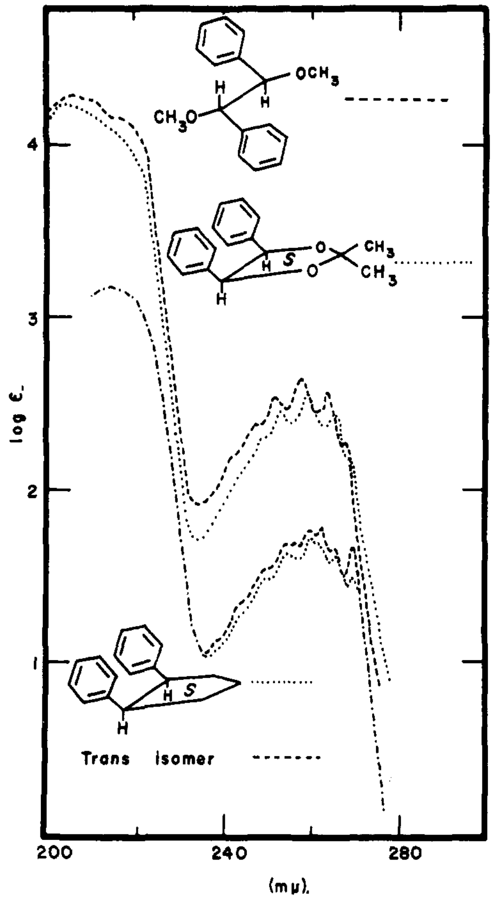
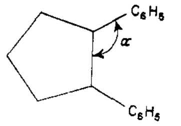
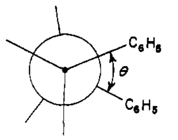


Fig. 5.—Ultraviolet absorption spectra of *cis* and *trans* isomers of disubstituted five-membered ring compounds in 95% ethanol (Cary recording spectrophotometer, model PMS). The lower pair of curves are displaced downward on the ordinate axis by 1.0 log ε unit.

That considerable repulsive forces operate tending to prevent two phenyls from becoming eclipsed is clear from the values of the equilibrium constants obtained between *meso*- and *dl*-1,2-dihydroxydibenzyl and their respective acetonides (XXVII and XXVIII), K_{dl}/K_{meso} being equal to 20.[27] Since the equilibrium constants between diastereomerically related substances such as *meso*- and *dl*-1,2-dihydroxydibenzyl are undoubtedly close to unity,[28] the ΔF^0 for *cis*-acetonide → *trans*-acetonide amounts to about -1.8 kcal. The question arises as to just how deformed the bond angles in a molecule such as *cis*-1,2-diphenylcyclopentane or XXVII have to become before the 1-carbons of each phenyl are separated by 3.4 Å. This condition is met if α is expanded from its normal 109 to 115° (the analogous bond angle in the paracyclophane with $m = n = 2$ is distorted similarly), and θ (see diagram) is adjusted to 75° by distorting the five-membered rings from the planar configuration. Similarly, if α is 120°, θ must be 56° if the 1-carbons of each phenyl are separated by 3.4 Å. On the other hand, to get the 1-carbons of the two phenyls





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(23) Samples of these compounds were very generously supplied by Dr. H. A. Weidlich [see *Ber.*, **71B**, 1601 (1938)].

(24) J. G. Aston, H. L. Fink and S. C. Schumann, THIS JOURNAL, **65**, 341 (1943).

(25) (a) K. S. Pitzer, *Science*, **101**, 672 (1945); (b) J. E. Kilpatrick, K. S. Pitzer and R. Spitzer, THIS JOURNAL, **69**, 2483 (1947).

(26) J. Donohue and K. N. Trueblood, *Acta. Cryst.*, **5**, 419 (1952).

(27) P. H. Hermans, *Z. Physik. Chem.*, **113**, 337 (1924).

(28) F. A. Abd Elhafez and D. J. Cram, THIS JOURNAL, **75**, 339 (1953).

3.0 Å. apart, if α is 115° then θ must be 37°. The actual dimensions in *cis*-1,2-diphenylcyclopentane probably lie somewhere nearer the last values, which would place the 1-carbons of each benzene ring farther apart than the distance calculated for the 1-carbons (2.84 Å.) of the paracyclophane with $m = 3$, $n = 4$, whose ultraviolet absorption spectrum is still far from normal.

The above considerations suggest that both the lack of planarity of the aromatic rings and transannular resonance effects operate in the smaller paracyclophanes to give them their abnormal ultraviolet absorption spectra. Transannular activating and deactivating influences and directive effects of functions substituted for hydrogen in the smaller paracyclophanes are currently under investigation.

The Infrared Spectra of the Paracyclophanes.—The principal bands found in the infrared spectra of the paracyclophanes I have been recorded.[29] In I with $n = m = 2$, strong bands appeared at 6.30, 10.75 and 11.20 μ which do not appear in the open-chain model compounds.[3a] Similar bands, though of lesser intensity, were found also in the compounds with $m = 2$, $n = 3$ or 4.[3a] The bands near 6.3 μ in these smaller cycles might possibly be due to an anomalous >C═C< stretching. The cycles with $m > n > 3$ show no unusual bands below 9 μ which are consistent throughout the series, the structural feature responsible for nearly every band in this region being known. Some of the bands above 9.0 μ are of diagnostic value for the cycles.

Experimental

p-**Acetyl-*p*′-carboxy-1,3-diphenylpropane (VII).**—To a solution prepared from 100 ml. of nitrobenzene, 33.9 g. (0.256 mole) of anhydrous aluminum chloride and 7.85 g. (0.077 mole) of acetic anhydride was added in one portion 16.8 g. (0.070 mole) of *p*-carboxy-1,3-diphenylpropane.[3d] The mixture was stirred at room temperature for 5 minutes, then at 50–60° for 2 hours. The cooled reaction mixture was then poured onto 150 g. of ice. After 50 ml. of concentrated hydrochloric acid had been added, the mixture was extracted with ether, and the ether extracts were washed and dried. After evaporation of the ether, the nitrobenzene was distilled at 1 mm., and the residual brown solid was taken up in 100 ml. of hot benzene. The hot solution was treated with decolorizing charcoal, filtered and diluted with a little hexane. Upon cooling, a colorless crystalline solid separated, wt. 16.0 g. (80%), m.p. 137.5–140.5°. For analysis a small sample was recrystallized three times, needles, m.p. 143.5–145.0°.

Anal. Calcd. for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.33; H, 6.41.

p-**Carbomethoxy-*p*′-carbomethoxymethyl-1,3-diphenylpropane (VIII).**—The keto acid VII, 50 g. (0.177 mole), was heated under reflux with 17.0 g. (0.530 mole) of sulfur in 200 ml. of morpholine for 10 hours. The excess morpholine was then distilled at reduced pressure, and to the residue was added a solution of 45 g. of potassium hydroxide in 600 ml. of 80% ethanol. The mixture was heated under reflux for 24 hours, then the ethanol was distilled with the simultaneous addition of an equal volume of water. The warm solution was then acidified and cooled, and the crude acid was filtered. After being dried, this material was esterified by heating under reflux for one hour with 500 ml. of methanol and 28 ml. of concentrated sulfuric acid. The cooled solution was then poured into water, and the product was extracted with ether. The ether extracts were washed with water and dilute sodium bicarbonate and were dried. After removal of the ether, the product was distilled to give a yellow oil, b.p. 160–200° (1 mm.). The distillate was heated under reflux with 2 g. of Raney nickel in 150 ml. of methanol for 1 hour. The nickel was removed by filtration, and the solvent was evaporated. The residue was distilled through a 2-foot column of the Podbielniak type, and after a 2-g. forerun, the desired ester was collected as a colorless liquid, b.p. 241–243° (4 mm.), n^{25}D 1.5509, wt. 30.1 g. (52%).

Anal. Calcd. for $C_{20}H_{22}O_4$: C, 73.60; H, 6.80. Found: C, 73.40; H, 6.79.

p-**Carboxy-*p*′-carboxymethyl-1,3-diphenylpropane.**—Saponification of the ester VIII gave the acid, yield 90%. Crystallization of this material from aqueous acetic acid gave a crystalline powder, m.p. 215–217°.

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08. Found: C, 72.27; H, 6.23.

p-**Carbomethoxy-*p*′-carbomethoxymethyl-1,3-dicyclohexylpropane (IX).**—The aromatic ester VIII, 27.4 g., was hydrogenated with 2 g. of platinum oxide in 75 ml. of pure acetic acid, the theoretical amount of hydrogen being taken up in 14 hours. The catalyst was removed from the solution by filtration, and, after evaporation of the solvent, the product was distilled, b.p. 216–219° (4 mm.), n^{25}D 1.4779, wt. 27.1 g. (95%).

Anal. Calcd. for $C_{20}H_{34}O_4$: C, 70.97; H, 10.13. Found: C, 71.24; H, 10.21.

p,*p*′-**Trimethylene-1,3-dicyclohexylpropane (XI).**—The acyloin reaction was carried out with the ester IX using the high-dilution apparatus described previously.[3a] To a suspension of 9.10 g. (0.395 mole) of sodium in 1.5 liters of xylene was added during 36 hours a solution of 26.7 g. (0.079 mole) of the ester in 500 ml. of xylene. After an additional hour of heating and stirring, the reaction mixture was cooled, and excess acetic acid was added, followed by sufficient water to dissolve the sodium acetate. Filtration of the mixture furnished 2 g. of a sticky yellow polymer. The organic phase in the filtrate was separated and dried. Removal of the solvent and distillation of the residue gave a very viscous yellow liquid, b.p. 205–235° (2 mm.), n^{25}D 1.5041, wt. 3.6 g. The pot residue weighed 20 g.

Anal. Calcd. for $C_{18}H_{30}O_2$: C, 77.65; H, 10.86. Found: C, 78.01; H, 10.99.

The crude acyloin X was not purified, but was converted directly to the hydrocarbon. To a mixture of 38 g. of amalgamated zinc[3c] and 100 ml. each of acetic and concentrated hydrochloric acid was added 3.6 g. of the crude acyloin. The mixture was heated under reflux for 30 hours, 15-ml. portions of concentrated hydrochloric acid being added at 12-hour intervals. The mixture was then poured into water and extracted with pentane, and the pentane extracts were washed, dried and concentrated to a volume of 10 ml. The solution was adsorbed on a 30-g. column of neutral alumina of activity I.[30] The column was washed with pentane, 25-ml. fractions being collected. Fractions 1 through 4 contained a total of 1.47 g. of a colorless oil. This material was hydrogenated with 0.04 g. of platinum oxide in acetic acid–ethyl acetate, thereby converting olefinic side-products to the desired saturated hydrocarbon.[3c] The hydrogenation was complete in 30 minutes, 19.5 ml. (corrected to standard conditions) of hydrogen having been absorbed. The solution was filtered and diluted with pentane and water. The pentane phase was separated, washed free of acetic acid and dried. The product was freed of solvent (in vacuum), and the oil (1.23 g.) was chromatographed on 40 g. of alumina (act. I)[30] with pure pentane, 25-ml. fractions being taken. Fractions 1 and 2 contained 0.82 g. of a white solid. Fractions 3 and 4 contained 0.01 g. of an oil which was discarded. Fractions 5 and 6 (eluted with ether) gave 0.32 g. of an oil which was distilled, n^{25}D 1.4806. The infrared spectrum of this material was similar to, but not identical with, that of the starting ester.

The solid from fractions 1 and 2 was crystallized from ethanol–ethyl acetate to yield 0.29 g., m.p. 96–112°, and a second crop, 0.08 g. of a solid, m.p. 87–100°. Two recrystallizations of the first crop and four of the second crop gave the pure hydrocarbon XI, needles, m.p. 115.0–116.2°, wt. 0.19 g. (1% from the ester IX).

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(29) Material supplementary to this article has been deposited as Document number 4303 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting in advance $1.25 for photoprints or $1.25 for 35 mm. microfilm payable to, Chief, Photoduplication Service, Library of Congress.

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

Anal. Calcd. for $C_{18}H_{32}$: C, 87.02; H, 12.98. Found: C, 87.06; H, 13.10.

p,p'-Trimethylene-1,3-diphenylpropane (XII).—The saturated hydrocarbon XI, 0.148 g. (0.00059 mole), was heated with 15 mg. of palladium-on-carbon for 1.5 hours at 250–320°, 69 ml. (27°) or 78% of the theoretical amount of hydrogen being evolved (the evolution of hydrogen ceased during this time). The residue was dissolved in pentane, the solution was filtered and the pentane was evaporated to yield a white solid, m.p. 82–94°, wt. 0.14 g. This material was chromatographed on 15 g. of alumina (act. I)[30] with pentane, 10-ml. fractions being taken. Fraction 1 contained 15 mg. of a white solid, m.p. 74–103°. Fraction 2 was empty. Fractions 3 through 9 contained a total of 100 mg. of a white solid, m.p. 85–93°. This material was crystallized from aqueous ethanol to give plates, 37.4 mg. (27%), m.p. 103.0–105.1°. Recrystallization of these plates from ethanol raised the melting point to 104.3–105.3°, wt. 32.6 mg.

Anal. Calcd. for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found: C, 91.51; H, 8.47.

Large crystals were obtained by allowing a solution of 10 mg. of the compound in 0.2 ml. of benzene to evaporate to dryness at room temperature. The density of a crystal was determined by flotation in aqueous sodium chloride after wetting with alcohol to give d. = 1.156 g./cc.

p-Hydroxymethyl-p'-(β-hydroxyethyl)-1,3-diphenylpropane.—The diester VIII, 27.7 g., in 100 ml. of ether was added dropwise to a suspension of 8.9 g. of lithium aluminum hydride in 200 ml. of ether. The mixture was stirred for an additional 0.5 hour, and then the excess reducing agent was decomposed by addition of ethyl acetate. After acidifying the mixture with dilute hydrochloric acid, the ether phase was separated, washed and dried. Evaporation of the ether and crystallization of the residue from benzene–hexane gave white needles, m.p. 87.8–88.9° (unchanged upon recrystallization), wt. 18.3 g. (80%).

Anal. Calcd. for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 80.01; H, 8.14.

p-Bromomethyl-p'-(β-bromoethyl)-1,3-diphenylpropane (XIII).—The above diol was converted to the dibromide with anhydrous hydrogen bromide at 100–110°[31] (90% yield). For analysis a sample was distilled without ebullition (bath 170° at 0.5 mm.) and crystallized from pentane at −80° to yield needles, m.p. 63.5–64.5°.

Anal. Calcd. for $C_{18}H_{20}Br_2$: C, 54.57; H, 5.09. Found: C, 54.37; H, 5.38.

***meso*-1,2-Dimethoxy-1,2-diphenylethane (XXIX).**—The reduction of benzoin with lithium aluminum hydride[32] furnished the *meso*-glycol, m.p. 135.3–135.9°, reported m.p. 136°.[27]

The dimethyl ether was obtained with methyl iodide and silver oxide, m.p. 141.0–142.1°, reported[33] m.p. 142°.

The acetonide XXVII was obtained by the usual method,[34] m.p. 58.5–59.5°, reported[27] m.p. 62°.

1,3-Bis-(4-carboxyamidomethylphenyl)-propane.—1,3-Bis-(4-carboxymethylphenyl)-propane,[3a] 10.0 g. (0.032 mole), and $SOCl_2$, 30 g. (0.25 mole) were held at 50–70° for 2 hours and then heated under reflux for 4 hours. The excess $SOCl_2$ was then evaporated in a vacuum, and the residue was taken up in 50 ml. of dry ether. The insoluble starting acid, 1.4 g., was removed by filtration. The solution containing the acid chloride was then added dropwise during ten minutes to 100 ml. of concentrated aqueous NH_4OH with cooling in an ice–salt-bath. The ether was removed by warming on a steam-bath and, after cooling, the product was collected, 8.5 g., m.p. 274–280°. The crude material was recrystallized from acetic acid (charcoal) to furnish white plates, m.p. 286.5–289.5°, wt. 5.5 g. (64% based on starting acid not recovered). An analytical sample was recrystallized seven times, fine needles, m.p. 291–293°.

Anal. Calcd. for $C_{19}H_{22}O_2N_2$: C, 73.52; H, 7.15; N, 9.03. Found: C, 73.55; H, 7.01; N, 9.20.

1,3-Bis-(4-cyanomethylphenyl)-propane (XVIII).—The amide, 143 g. (0.461 mole), and PCl_5, 90 g. (0.432 mole), were intimately mixed by grinding together, and the mixture was heated for one hour at 110–120° at 35 mm. The resulting dark red melt was taken up in chloroform, and the solution was filtered free of insoluble material. The chloroform solution was then treated with charcoal and filtered. The filtrate was washed with 10% sodium hydroxide solution and water and, after drying, the chloroform was evaporated. The dark red oil was taken up in hot ethanol, and the solution was decanted from the insoluble tar. The ethanol was removed, the residue was dissolved in 2 liters of benzene and the resulting solution was poured through a column of 200 g. of basic alumina. The column was washed with an additional 2 liters of benzene, the benzene solutions were combined and the solvent was removed. The residue was then distilled to yield a yellow oil which solidified on standing, wt. 48 g., b.p. 206–212° (0.2 mm.). Two crystallizations of this material from ethanol gave white needles, m.p. 72–74°, wt. 35 g. (28%). An analytical sample melted at 72.5–74°.

Anal. Calcd. for $C_{19}H_{18}N_2$: C, 83.17; H, 6.61. Found: C, 83.30; H, 6.64.

γ-(p-Succinylphenyl)-butyric Acid (XIX).—β-Benzoylpropionic acid[35] was converted to γ-phenylbutyric acid by a modified Wolff–Kishner reduction, yield 95%, b.p. 141–145° (3.5 mm.), solidified on standing (reported[36] m.p. 46–47°, b.p. 125–130° (3 mm.)). The ethyl ester was prepared in 90% yield with ethanol and sulfuric acid, b.p. 111–113° (3 mm.) (reported[37] b.p. 130–131° (10 mm.)).

In one liter of tetrachloroethane at −10° were dissolved, in order, 215.5 g. (1.12 moles) of ethyl γ-phenylbutyrate, 123 g. (1.23 moles) of succinic anhydride and 494 g. (3.70 moles) of aluminum chloride (the latter in 50-g. portions). The temperature of the mixture was kept in the range of −10 to 0° throughout the addition period and for an additional 0.5 hour. After standing at room temperature for 36 hours, excess 2 *N* hydrochloric acid was added to the mixture (temperature kept below 25°), and the solvent was steam distilled. The residual oil solidified upon cooling and was filtered to give a brown crystalline solid. The wet crude material was dissolved in boiling excess 10% sodium carbonate solution, and the alumina was removed by filtering the hot solution through Celite. The solution was then cooled somewhat, 25 g. of potassium hydroxide was added, and the resulting solution was heated under reflux for 0.5 hour. The solution was then cooled and acidified, and the product was collected, 293 g. (99%), m.p. 158–161°. An analytical sample was purified by two crystallizations from aqueous acetic acid, white granules, m.p. 164.0–164.5°.

Anal. Calcd. for $C_{14}H_{16}O_5$: C, 63.62; H, 6.10; neut. equiv., 132. Found: C, 63.31; H, 6.29; neut. equiv., 130.

p-Bis-(γ-carboxypropyl)-benzene.—The keto acid XIX, 293 g., was reduced by the modified Wolff–Kishner method to yield 258 g. (94%) of the crude diacid, m.p. 171–175°. For analysis a small sample was recrystallized three times from aqueous acetic acid, plates, m.p. 176.0–177.0°.

Anal. Calcd. for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25; neut. equiv., 125. Found: C, 67.29; H, 7.36; neut. equiv., 129.

p-Bis-(γ-carbomethoxypropyl)-benzene (XX).—The diacid, 50.2 g., was esterified with methanol and sulfuric acid. After the usual work-up, the product was distilled through a 2-foot column of the Vigreux type at 3.5 mm. After a 1.8-g. forerun, the product was collected as a colorless liquid, b.p. 187.5–189.5°, wt. 43.3 g. (78%), $n^{25}D$ 1.4955.

Anal. Calcd. for $C_{16}H_{22}O_4$: C, 69.04; H, 7.97. Found: C, 69.33; H, 8.22.

1,4-Bis-(γ-carbomethoxypropyl)-cyclohexane (XXV).—The aromatic diester XX, 75.0 g., was hydrogenated with 2 g. of platinum oxide in 150 ml. of acetic acid. The hydrogen uptake was 98% of theoretical and was complete in 10 hours. The solution was filtered free of catalyst, the solvent was evaporated, and the product was distilled as a colorless liquid, b.p. 180–182° (4 mm.), $n^{25}D$ 1.4620, wt. 73.6 g. (92%).

Separation of the *cis* and *trans* Isomers of 1,4-Bis-(γ-carbomethoxypropyl)-cyclohexane (XXV).—The mixture of

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[31] E. E. Reid, J. R. Ruhoff and R. E. Burnett, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 246.

[32] L. W. Trevoy and W. G. Brown, THIS JOURNAL, **71**, 1675 (1949).

[33] J. C. Irvine and J. Weir, *J. Chem. Soc.*, **91**, 1384 (1907).

[34] H. G. Derx, *Rec. trav. chim.*, **41**, 312 (1922).

[35] L. F. Somerville and C. F. H. Allen, "Organic Syntheses," Col. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 81.

[36] E. L. Martin, *ibid.*, p. 499.

[37] J. von Braun, *Ber.*, **44**, 2867 (1911).

isomers obtained above, 53.8 g. ($n^{25}\mathrm{D}$ 1.4620), was partially crystallized from 40 ml. of pentane at −30°. The crystalline material, which melted below room temperature, was filtered and twice recrystallized from pentane at −50°. There was thus obtained 7.36 g. (14%) of prisms (*trans*-XXV), m.p. 28.4–29.2°, $n^{25}\mathrm{D}$ 1.4606 (supercooled liquid).

Anal. Calcd. for $C_{16}H_{28}O_4$: C, 67.57; H, 9.92. Found: C, 67.50; H, 9.75.

The filtrates remaining after the bulk of the *trans* isomer had been removed were combined and cooled at −50° for one hour. The small amount of solid was filtered and distilled to yield 0.72 g. of a colorless liquid, $n^{25}\mathrm{D}$ 1.4608. The solvent was removed from the filtrate, and the residual oil was distilled to furnish fairly pure *cis* isomer XXV, $n^{25}\mathrm{D}$ 1.4624, wt. 44.5 g.

Anal. Calcd. for $C_{16}H_{28}O_4$: C, 67.57; H, 9.92. Found: C, 67.38; H, 9.91.

***trans*-1,4-Bis-(γ-carboxypropyl)-cyclohexane.**—Saponification of 1.00 g. of the *trans*-ester XXV gave 0.85 g. of the *trans*-acid, m.p. 169.4–171.1°. Recrystallization of this material from aqueous acetic acid gave needles, m.p. 170.9–171.6°.

Anal. Calcd. for $C_{14}H_{24}O_4$: C, 65.60; H, 9.44. Found: C, 65.63; H, 9.62.

***cis*-1,4-Bis-(γ-carboxypropyl)-cyclohexane.**—Saponification of 0.30 g. of the *cis*-ester XXV gave 0.27 g. of the crude acid, m.p. 116.0–117.5°. This material was dissolved in hot acetic acid, and about one-fourth of the material was allowed to crystallize. The resulting powder was filtered, m.p. 116–135°. The filtrate was diluted with a little water and a second crop was taken, 0.1 g., fine needles, m.p. 116.4–117.4°. The latter is thought to be the pure *cis* isomer, although the possibility of a eutectic mixture has not been eliminated.

Anal. Calcd. for $C_{14}H_{24}O_4$: C, 65.60; H, 9.44. Found: C, 65.37; H, 9.61.

***p*-Bis-(δ-hydroxybutyl)-benzene.**—Reduction of diester XX with lithium aluminum hydride was accomplished in a manner similar to that described for the reduction of diester VIII. From 92.7 g. of XX there was thus obtained 63.0 g. (85%) of the diol, m.p. 60.5–62.4°. A small sample was crystallized from benzene to give plates, m.p. 62.0–63.0°.

Anal. Calcd. for $C_{14}H_{22}O_2$: C, 75.63; H, 9.98. Found: C, 75.76; H, 9.98.

***p*-Bis-(δ-bromobutyl)-benzene (XXI).**—The above diol (55.6 g.) was converted to the dibromide as described for the similar conversion leading to dibromide XIII. The product was distilled to give a colorless liquid, b.p. 195–199° (4 mm.), wt. 78.6 g. (90%). The compound solidified on standing, m.p. 35–38°. An analytical sample of XXI was twice recrystallized from alcohol, white needles, m.p. 39.5–40.5°.

Anal. Calcd. for $C_{14}H_{20}Br_2$: C, 48.30; H, 5.79. Found: C, 47.97; H, 5.80.

***p*-Bis-(5,5-dicarboxypentyl)-benzene.**—Sodiomalonic ester was prepared by dissolving 10.9 g. (0.475 mole) of sodium in 500 ml. of ethanol (dried with sodium and diethyl phthalate), adding 150 g. (0.94 mole) of ethyl malonate and heating the solution under reflux for 5 minutes. A mixture of 78.6 g. (0.226 mole) of dibromide XXI and 25 g. of ethyl malonate was added dropwise during 5 minutes, and the resulting mixture was heated under reflux for an additional 0.5 hour (neutral to phenophthalein). Water and benzene were then added, and the organic phase was separated, washed and dried. The volatile materials were removed by distillation with a final bath temperature of 150° (2.5 mm.). The residual tetra-ester was then saponified by heating under reflux for 2 hours with 114 g. of potassium hydroxide in 700 ml. of 80% ethanol. The cooled solution was diluted with water and acidified, and the white crystalline powder was collected, 96.0 g., m.p. 184–186° dec. For analysis a small sample was crystallized from water to yield plates, m.p. 185.0–186.5° dec.

Anal. Calcd. for $C_{20}H_{26}O_8$: C, 60.90; H, 6.65. Found: C, 60.73; H, 6.88.

***p*-Bis-(5-carboxypentyl)-benzene.**—The crude tetra-acid (see above), 96.4 g., was decarboxylated by heating at 185–200° for 1 hour. The crude acid thus obtained, 75.1 g., had m.p. 105–111°. A sample was twice crystallized from acetic acid, needles, m.p. 126.5–127.4°.

Anal. Calcd. for $C_{18}H_{26}O_4$: C, 70.56; H, 8.55. Found: C, 70.63; H, 8.66.

***p*-Bis-(5-carbomethoxypentyl)-benzene (XXII).**—Esterification of the above acid (75.1 g.) with methanol and sulfuric acid was accomplished in the usual way, and the product was distilled through a 2-foot Podbielniak-type column. After a 2.9-g. forerun the desired ester distilled as a colorless liquid, b.p. 224.5–226.5° (4.5 mm.), $n^{25}\mathrm{D}$ 1.4918, wt. 48.4 g. (64% from dibromide XXI).

Anal. Calcd. for $C_{20}H_{30}O_4$: C, 71.82; H, 9.04. Found: C, 71.91; H, 9.27.

6-Hydroxy-7-keto-1,12-*p*-phenylenedodecane (XXIII).—The acyloin reaction was carried out with 15.0 g. of ester XXII in a manner similar to that described for ester IX. The product was distilled through a 2-foot Podbielniak-type column, and after a 0.41-g. forerun, the acyloin was collected as a yellowish liquid, b.p. 192.5–194° (3.5 mm.), wt. 8.49 g. The compound solidified upon standing, m.p. 41–44°. A small sample was crystallized from pentane at −80°, white prisms, m.p. 46.0–47.0°. The infrared spectrum showed strong bands at 2.84 and 5.82 μ characteristic of —OH and C=O stretching, respectively.

Anal. Calcd. for $C_{18}H_{26}O_2$: C, 78.79; H, 9.55. Found: C, 78.86; H, 9.66.

***p*-Dodecamethylenebenzene (XXIV).**—The acyloin XXIII, 10.00 g., was reduced with zinc and acid as described for the preparation of hydrocarbon XI. The reaction mixture was then poured into water and extracted with pentane. The pentane extracts were washed, dried and the pentane was evaporated. The resulting oil was dissolved in a mixture of 60 ml. of ethyl acetate and 100 ml. of ethanol. After addition of 0.2 g. of platinum oxide, the material was hydrogenated, 16 ml. of hydrogen (S.T.P.) was taken up in 20 minutes. The catalyst was removed by filtration, the solvent was evaporated and the product was distilled as a colorless liquid, b.p. 150–155° (3.5 mm.), $n^{25}\mathrm{D}$ 1.5218, wt. 7.64 g. This material was then distilled through a 2-foot Podbielniak-type column at 5.5 mm. The first three fractions (5.51 g. or 62% combined) had constant refractive indices and boiling points; $n^{25}\mathrm{D}$ 1.5204, b.p. 163.5–164.5°.

Anal. Calcd. for $C_{18}H_{28}$: C, 88.45; H, 11.55. Found: C, 88.30; H, 11.68.

Two additional distillation fractions also were collected, b.p. 164.5–165.5°, $n^{25}\mathrm{D}$ 1.5223, wt. 0.84 g., and b.p. 165.5–174°, $n^{25}\mathrm{D}$ 1.5290, wt. 0.97 g., respectively. The infrared and ultraviolet spectra of all of the distillation fractions were identical.

Attempted Acyloin Cyclization of *cis*-1,4-Bis-(γ-carbomethoxypropyl)-cyclohexane (XXV).—The experimental procedure was similar to that used for the cyclization of ester IX. The *cis*-ester XXV, 33.0 g. (0.11 mole), in 300 ml. of xylene was added to 13.4 g. (0.58 mole) of sodium suspended in 1500 ml. of xylene during 24 hours. After decomposition of the reaction mixture, the solution was filtered free of a trace of polymer (20 mg.), and xylene phase was washed and dried. After removal of the solvent the residue was distilled to furnish starting material as a slightly yellowish oil, b.p. 178–181° (4 mm.), $n^{25}\mathrm{D}$ 1.4628, wt. 29.3 g. (89%).

Attempted Acyloin Cyclization of *trans*-1,4-Bis-(γ-carbomethoxypropyl)-cyclohexane (XXV) and *p*-Bis-(γ-carbomethoxypropyl)-benzene (XX).—The experimental procedure was analogous to that described for *cis*-XXV. In a like manner there was recovered 89% of the starting material with *trans*-XXV and 84% of the starting material with the aromatic ester XX. The latter also was subjected to the same reaction conditions using sodium–potassium alloy and was recovered likewise.

Attempted Acyloin Cyclization with Acid Chloride XXVI.—The acid chloride was prepared by allowing 26.7 g. of *cis*-1,4-bis-(γ-carboxypropyl)-cyclohexane to react with 49.5 g. of thionyl chloride at room temperature for 3 hours, followed by one hour on the steam-bath. Distillation of the resulting material gave a colorless liquid, b.p. 190–194° (7 mm.) with appreciable decomposition, wt. 17.0 g.

The acid chloride was then allowed to react with sodium in a manner similar to that described for the *cis*-diester XXV. After decomposition of the reaction mixture, filtration of the solution yielded an amorphous brown powder. This material was ground under water in a mortar, filtered and washed with water. Upon heating to 140° in an oven, the wet material ignited.

The xylene phase was freed of solvent, the residue was distilled at 2 mm., and the distillate was collected in two fractions: (1) b.p. 200–210°, a yellow oil, $n^{25}\text{D}$ 1.4877, wt. 0.7 g.; (2) b.p. 210–240°, a yellowish solid, wt. 1.5 g. Both of these fractions gave negative acyloin tests.[38]

***p,p'*-Tetramethylene-1-phenyl-4-cyclohexylbutane** (II, $m = n = 4$).—*p,p'*-Tetramethylene-1,4-diphenylbutane,[3c] 0.95 g. (0.0036 mole), was hydrogenated with 0.1 g. of PtO_2 in a mixture of 10 ml. of glacial acetic acid and 20 ml. of ethyl acetate. The theoretical amount of hydrogen was absorbed in 4 hours and the reaction was stopped. The solution was filtered free of catalyst and was poured into pentane. The pentane phase was washed, dried and the solvents were removed in vacuum. The residual oil was dissolved in pentane and adsorbed on a 125-g. column of alumina (act. I).[30] The column was washed with pure pentane, and the eluate was collected in 25-ml. fractions. Fractions 1–3 contained nothing, fraction 4 contained 0.08 g. of oil. Fractions 3–6 contained 0.70 g. of the desired product, and fractions 9–12 (eluted with ether) gave 0.17 g. of recovered starting material. The product in fractions 3–6, 0.70 g. (71%), had m.p. 47.8–48.4°. For analysis a sample was crystallized from ethanol, needles, m.p. 48.0–48.6°.

Anal. Calcd. for $C_{20}H_{30}$: C, 88.82; H, 11.18. Found: C, 89.04; H, 11.10.

***p,p'*-Trimethylene-1-cyclohexyl-4-phenylbutane** (II, $m = 3$, $n = 4$).—The reaction and work-up were carried out in a manner similar to that described for the homolog (II, $m = n = 4$). From 150 mg. of the paracyclophane was obtained 25 mg. (16%) of the pure product, needles, m.p. 31.4–32.1°.

Anal. Calcd. for $C_{19}H_{28}$: C, 88.99; H, 11.01. Found: C, 88.80, 88.54; H, 10.34, 10.95.

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[38] W. Rigby, *J. Chem. Soc.*, 793 (1951).

[CONTRIBUTION FROM THE MEDICAL RESEARCH LABORATORY, VETERANS ADMINISTRATION HOSPITAL, AND THE DEPARTMENT OF CHEMISTRY, BAYLOR UNIVERSITY COLLEGE OF MEDICINE]

Studies in the Naphthalene Series. I. Oxidative Coupling of 1-Naphthol

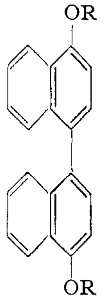
BY J. D. EDWARDS, JR., AND J. L. CASHAW

RECEIVED MAY 21, 1954

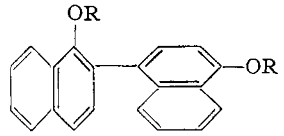
The structure V, 2,2'-bi-1-naphthol, assigned to one of the oxidation products of 1-naphthol has been shown to be correct. All possible interconversions between this binaphthol and its mono- and dimethyl ether have been made. A study of the ultraviolet absorption spectra of the various binaphthyls prepared is presented.

The oxidative coupling of 1-naphthol by means of ferric chloride was first reported by Dianin.[1] That 4,4'-bi-1-naphthol (I) is formed has been shown,[2–4] but it was only recently[5] that a second product was isolated from this reaction and assigned the structure 2,2'-bi-1-naphthol (V) (m.p. 220°).[6] The evidence presented in support of structure V by Ioffe was convincing but not conclusive.

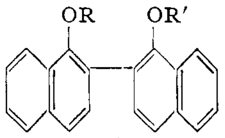
Since we were interested in the synthesis of certain substituted 2,2'-bi-1-naphthols by oxidation of the appropriate 1-naphthols, it was desirable to prove the structure of the oxidation product V of 1-naphthol reported by Ioffe and study some of its reactions.



I, R = H
II, R = CH_3



III, R = H
IV, R = CH_3



V, R = R' = H
VI, R = H; R' = CH_3
VII, R = R' = CH_3

The synthesis of the dimethyl ethers of the three binaphthols, 4,4'-, 2,4'- and 2,2'-bi-1-naphthol (I, III and V) expected from the oxidative coupling of 1-naphthol, was realized by application of the Ullmann reaction. 4,4'-Dimethoxy-1,1'-binaphthyl (II) was formed by the coupling of 4-iodo-1-methoxynaphthalene or from 4-bromo-1-methoxynaphthalene.[7] The product proved to be identical with that obtained by the methylation[2,8] of I which was isolated from the oxidation of 1-naphthol. The identity of this product[2–4] establishes the structure of 4-bromo- and 4-iodo-1-methoxynaphthalene. The 4-iodo-1-methoxynaphthalene was prepared by the interaction of 1-methoxynaphthalene and iodine monochloride.

The synthesis and coupling of 2-iodo-1-methoxynaphthalene were carried out according to the directions of Clemo[3] and gave 1,1'-dimethoxy-2,2'-binaphthyl (VII); mol. wt. (Rast), 300.

From the coupling of a mixture of 2- and 4-iodo-1-methoxynaphthalenes, three compounds were isolated by fractional crystallization. It was shown that two of these were identical with II and VII. The remaining one was therefore 1,4'-dimethoxy-1',2-binaphthyl (IV).

The complete methylation of V proved to be quite difficult. It was accomplished by repeatedly using large excesses of potassium hydroxide and dimethyl sulfate in diethylene glycol as a solvent. The product was identical with synthetic VII. The structure V postulated by Ioffe[5] for the binaphthol obtained from the oxidation of 1-naphtho-

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[1] A. P. Dianin, *J. Russ. Phys. Chem., Soc.*, **6**, 187 (1874).

[2] A. Corbellini and E. Debenedetti, *Gazz. chim. ital.*, **59**, 391 (1929).

[3] G. R. Clemo, J. G. Cockburn and R. Spence, *J. Chem. Soc.*, 1265 (1931).

[4] W. M. Cumming and G. Howie, *ibid.*, 528 (1932).

[5] I. S. Ioffe and B. K. Kirchevtsov, *J. Gen. Chem.* (*USSR*), **9**, 1136 (1939).

[6] Apparently Ioffe[5] was unaware of the work by Clemo[3] who had synthesized 1,1'-dimethoxy-2,2'-binaphthyl (VII) and on demethylation obtained V (m.p. 212°), and of W. M. Cumming and G. D. Muir, *J. Roy. Tech. Coll.* (*Glasgow*), **4**, 61 (1937); *C. A.*, **31**, 4310 (1937), who obtained a compound postulated as V (m.p. 213°) by the alkaline fusion of 2,2'-binaphthyl-1,1'-disulfonic acid.

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[8] E. Ostermayer and J. Rosenhek, *Ber.*, **17**, 2453 (1884).