

hydrocarbons were diluted with anhydrous ether before injection, and retention times were calculated from the ether peak. The columns were operated at 160°. Separation and identification of the various isomers were demonstrated with authentic samples.

Treatment of Pentylbenzenes with Aluminum Chloride.—In all experiments the pentylbenzene, water-activated aluminum chloride and benzene (in the proportions specified in Tables I and II) were stirred continuously by means of a Teflon-covered magnetic stirrer in a flask equipped with an efficient reflux condenser

protected by a calcium chloride tube. At the conclusion of the reaction, the flask was cooled and water was added cautiously through the condenser. The organic layer was separated, the water layer was washed with three portions of ether, and these were combined with the organic layer. The ether solution was washed with 10% sodium bicarbonate solution and water, dried over calcium chloride, and distilled through an 80-cm. Nichrome spiral column. The pentylbenzene fraction which was analyzed was usually about a 10° cut. Results of the analyses are given in Tables I and II.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE STATE UNIVERSITY, DETROIT 2, MICH.]

The Molecular Structure and Electronic Spectrum of [8]Paracyclophane. A New Synthetic Method for the Preparation of Strained Large Rings^{1,2}

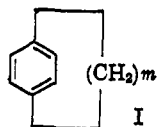
BY NORMAN L. ALLINGER, LESLIE A. FREIBERG, ROBERT B. HERMANN AND MARY ANN MILLER

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The synthesis of the [8]paracyclophane ring system by a ring contraction *via* the photolysis of an α -diazoketone is described. The ultraviolet spectrum of the compound was calculated by the method of Pariser and Parr for various degrees of non-planarity of the aromatic ring. The observed spectrum shows shifts relative to a planar ring which are similar to those calculated, which allows an estimate of the degree of non-planarity of the ring to be made.

Introduction

A number of compounds are known which contain benzene rings that are seriously distorted from their regular hexagonal geometry by steric constraints.³ Perhaps the simplest case in which an attempt has been made to study systematically a series of compounds in which the distortion of the ring is progressively increased is that of the paracyclophanes (I).^{4,5} These compounds are known for $m = 12$,⁴ 10,⁴ 9,^{4,6} and 8.⁵ When m is 10 or greater, the electronic properties of the aromatic ring are essentially indistinguishable from



those of an open chain analog, but as m is decreased the ultraviolet spectra become abnormal, and models suggest that this abnormality may be associated with the sterically induced non-planarity of the aromatic ring. While [9]paracyclophane has been known for many years,⁶ the procedure by which it was prepared did not lead successfully to the next smaller homolog. The objectives of this work were to prepare the [8]paracyclophane by a general synthetic method developed for the purpose, and to study the properties of the compound, both experimentally and theoretically.

While this work was in progress Cram and Knox reported an elegant synthesis of [8]paracyclophane.⁵ The synthetic method used in the present work, while more laborious and less imaginative, does appear to offer the advantage of greater generality.

(1) A preliminary communication of some of the results of this work has been published; *J. Org. Chem.*, **27**, 1490 (1962).

(2) This work was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

(3) For example the [2.2]paracyclophane (C. J. Brown, *J. Chem. Soc.*, 3265 (1953)); and the [2.2]metacyclophane (C. J. Brown, *ibid.*, 3278 (1953)).

(4) D. J. Cram, N. L. Allinger and H. Steinberg, *J. Am. Chem. Soc.*, **76**, 6132 (1954), and earlier papers.

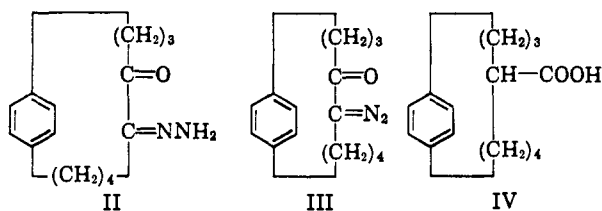
(5) D. J. Cram and G. R. Knox, *ibid.*, **83**, 2204 (1961).

(6) M. F. Bartlett, S. K. Figdor and K. Wiesner, *Can. J. Chem.*, **30**, 291 (1952).

(7) Subsequent to completion of this work, A. T. Blomquist and F. W. Schlaefer, *J. Am. Chem. Soc.*, **83**, 4547 (1961), independently reported the application of this method to the preparation of other medium rings, and mentioned that [8]paracyclophane-4-carboxylic acid had also been obtained by this method by L. Chow.

Results

In general a cyclic structure can be synthesized by ring closure, by ring contraction or by ring expansion. The first of these methods has previously failed to yield [8]paracyclophane, the last looked unpromising and the method of ring contraction was therefore considered. The photolysis of an α -diazoketone is a type of Wolff rearrangement which has recently been shown to yield ring contraction of small rings, even when the product being formed is highly strained.⁸ Since 4,5-diketo-[9]paracyclophane (II) monohydrazone was a known compound,⁹ the reaction sequence shown was considered worth investigating.



Compound II (prepared by a straightforward but lengthy sequence⁹ which began with γ -phenylbutyric acid and involved an acyloin ring closure as a key step) was oxidized¹⁰ with manganese dioxide and gave III. The latter was not isolated, but was identified in solution by strong absorption bands in the infrared at 2030 and 1640 cm^{-1} . Irradiation of III gave IV (25% yield from II). The structure of IV was established by analysis, by the fact that from the infrared spectrum the compound was a carboxylic acid, and by the analysis of the *p*-bromophenacyl ester, which showed the compound to be monomeric.

The proton magnetic resonance spectrum of the compound was also informative, and showed resonance at: -1.70τ (COOH), $+2.95 \tau$ (Ar-H), and a poorly resolved group of peaks at 7.15, 7.62, 8.50 and 9.35 τ . According to the theory of aromatic ring currents,¹¹

(8) (a) L. Horner and E. Spietschka, *Ber.*, **88**, 934 (1954); (b) M. P. Cava, R. L. Little and R. D. Napier, *J. Am. Chem. Soc.*, **80**, 2257 (1958); (c) J. Meinwald and P. Gassman, *ibid.*, **82**, 2857 (1960).

(9) D. J. Cram and M. F. Antar, *ibid.*, **80**, 3103 (1958).

(10) H. Morrison, S. Danishefsky and P. Yates, *J. Org. Chem.*, **26**, 2617 (1961).

(11) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 180.

the aliphatic hydrogens in the side chain which are over the center of the aromatic ring should show absorption at very high field, and the absorption at 9.35 τ must be from these hydrogens. If the ring current were seriously interfered with by the non-planarity of the ring, then it might be anticipated that the aromatic protons would show resonance at a higher field than otherwise. Actually it was found that *p*-diethylbenzene under similar conditions showed the aromatic resonance at 3.01 τ , and it seems likely that the effect of the carboxyl in the cyclophane in producing a downfield shift outweighs the sought for shift.

The Electronic Spectrum

Pariser and Parr have shown¹² that the ultraviolet (electronic) spectrum of benzene can be calculated to a fair approximation utilizing the idea¹³ of a core Hamiltonian and accounting for the interactions of the separate π -electrons with the core and with each other. The key to the solution of the problem lies in the empirical evaluation of certain integrals. Subsequently, Schiess and Pullman¹⁴ showed that with some small numerical modifications of the procedure, an excellent fit of the calculated values and the observable portion of the spectrum could be made. The latter calculations were based on the old value of the bond length (1.390 Å.) for benzene. It was hence thought desirable to repeat the calculation of Schiess and Pullman using the newer bond length^{15,16} of 1.397 Å. for benzene. One begins by assuming that the one-center repulsion integral γ_{11} , or (11|11), has the value 11.080 e.v.¹⁷ It is then necessary to evaluate the resonance integral, β_{12} . Schiess and Pullman did this by a reasonably straightforward but laborious solution of the theoretical equation (1)¹²

$$\beta_{pq} = \sum_{l \neq q} [S_{pq}(l:qq) + S_{pq}(l:qq) - (l:pq) - (l:pq)] + \sum_r [S_{pq}(r:qq) - (r:pq)] \quad (1)$$

and obtained $\beta_{12} = -2.402$ e.v. at $r = 1.390$ Å. Using this value of β_{12} , the value of γ_{12} (or [11|22]) was then adjusted so that when the other integrals were calculated in the usual manner,¹⁸ the calculated spectrum agreed with the experimental one. Using the theoretical eq. 1, β was calculated in the present work at 1.390 Å. for benzene, and the value -2.612 e.v. was obtained. (Pariser and Parr give a value of -2.39 e.v.) The reason for the discrepancy between the value determined in the present work and the earlier values is due mainly to different methods of evaluating the integral [11|12].¹⁹ However, any value of β in this range can be fit to the benzene spectrum by adjustment of γ_{12} , and since the theoretical value is probably not the best value anyway, what has been done in the present case is to accept the value -2.402 e.v., but to let it apply at 1.397 Å. When benzene is bent, the bond lengths become unequal, and it is necessary to know how β varies with distance. We have therefore calculated β_{12} for ethylene from eq. 1; -2.974 e.v. at

(12) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).

(13) M. Goepfert-Mayer and A. L. Sklar, *ibid.*, **6**, 645 (1938).

(14) P. Schiess and A. Pullman, *J. chim. phys.*, **53**, 101 (1956).

(15) A. Almenningsen, O. Bastiansen and L. Fernholt, *Kgl. Norske Videnskab. Selskabs. Skrifter*, No. 3, 1 (1958).

(16) A. Langseth and B. P. Stoicheff, *Can. J. Phys.*, **34**, 350 (1956).

(17) H. A. Skinner and H. O. Pritchard, *Trans. Faraday Soc.*, **49**, 1254 (1953).

(18) C. C. J. Roothaan, "Tables of Two-Center Coulomb Integrals between 1s, 2s and 2p Orbitals," Special Technical Report, Laboratory of Molecular Structure and Spectra, Department of Physics, University of Chicago, 1955.

(19) Schiess and Pullman (private communication) used the approximation [11|12] = $\frac{1}{2}S_{12}([11|11] + [11|22])$ (see R. S. Mulliken, *J. chim. phys.*, **46**, 497 (1949)) while in the present work the approximation [11|12] = $S_{12}[11|mm]$ where m , a hypothetical orbital half-way between 1 and 2 (see A. L. Sklar, *J. Chem. Phys.*, **7**, 984 (1939), was used.

TABLE I
QUANTITIES USED IN CALCULATION OF BENZENE AND BENT
BENZENE SPECTRA (θ = DEGREE OF BENDING)

Quantity	0°	15°	22.5°	30°
r_{12} (Å.)	1.397	1.398	1.399	1.400
r_{13}	2.4179	2.404	2.387	2.363
r_{14}	2.794	2.744	2.6854	2.604
r_{23}	1.397	1.394	1.393	1.392
r_{25}	2.794	2.794	2.795	2.796
r_{26}	2.4179	2.4214	2.4231	2.425
Integrals over atomic orbitals, e.v.				
γ_{12}	6.961	6.959	6.957	6.955
γ_{13}	5.6545	5.682	5.691	5.706
γ_{14}	4.954	5.038	5.140	5.287
γ_{23}	6.961	6.967	6.969	6.971
γ_{25}	4.954	4.954	4.952	4.951
γ_{26}	5.6545	5.651	5.647	5.643
β_{11}	11.080	11.080	11.080	11.080
β_{12}	-2.402	-2.289	-2.157	-1.975
β_{23}	-2.402	-2.419	-2.424	-2.430
α_1	-41.405	-41.540	-41.656	-41.829
α_2	-41.405	-41.433	-41.436	-41.446
Integrals over molecular orbitals, e.v.				
J_{11}	6.8775	6.8800	6.8944	6.9042
J_{12}	6.8775	6.8800	6.8923	6.9087
J_{13}	6.8775	6.8800	6.8923	6.8984
J_{22}	7.1624	7.1630	7.1620	7.1613
J_{23}	6.5926	6.5955	6.5898	6.5831
J_{33}	7.1624	7.1990	7.2410	7.3048
K_{12}	1.2388	1.2532	1.2717	1.2974
K_{13}	1.2388	1.2094	1.1776	1.1312
K_{14}	0.5697	0.5675	0.5683	0.5679
K_{15}	.5697	.5752	.5831	.5945
K_{16}	.5855	.5867	.5848	.5848
K_{23}	.2849	.2728	.2709	.2597
K_{24}	.6194	.6073	.5908	.5668
K_{25}	1.2049	1.2025	1.2015	1.2002
K_{34}	1.2049	1.2181	1.2314	1.2496
I_1	-46.209	-46.133	-46.000	-45.836
I_2	-43.807	-43.852	-43.860	-43.876
I_3	-43.807	-43.751	-43.657	-43.556
I_4	-39.003	-39.259	-39.516	-39.869
I_5	-39.003	-39.014	-39.012	-39.016
I_6	-36.601	-36.803	-37.011	-37.289

1.334 Å. From the two theoretical values ($\beta = -2.612$ e.v. at 1.390 Å.), a curve of the form $\beta = Ae^{-Br}$ was constructed. The constant A was then adjusted to give $\beta = -2.402$ e.v. at 1.397 Å., and eq. 2 was obtained.

$$\beta \text{ (e.v.)} = -61.232 \exp(-2.31813r) \text{ (Å.)} \quad (2)$$

Finally, the values for the two-center repulsion integrals are needed. For distances greater than 2.408 Å. theoretical values¹⁸ were used. For shorter distances a parabola (3) was fit to the three points available

$$\gamma_{pq} = 11.080 - 3.92327r + 0.69786r^2 \text{ (} r \leq 2.408 \text{ Å.)} \quad (3)$$

$\gamma_{11} = 11.080$ e.v., $\gamma_{12} = 6.961$ at 1.397 Å. (Schiess and Pullman's empirical value) and $\gamma_{12} = 5.679$ at 2.408 Å. (the theoretical value). Neglecting penetration integrals, the Coulomb integral for a core nucleus is given by (4)¹².

$$\alpha_p = W_p - \sum_{p \neq q} \gamma_{pq} \quad (4)$$

For carbon, $W_c = -11.22$ e.v. For benzene the wave functions are determined by symmetry (Table II). The data for the input matrices are given in Table I. The calculations were carried out following Pariser and Parr using an IBM 650 computer with previously described

TABLE II
 WAVE FUNCTIONS FOR BENZENE AND BENT BENZENE

θ	Symmetry	Orbital	x_1	x_2	x_3	x_4	x_5	x_6
0°	A _{2u}	ϕ_1	0.40825	0.40825	0.40825	0.40825	0.40825	0.40825
	E _{1g}	ϕ_2	-.00371	-.50184	-.49814	.00371	.50184	.49814
	E _{1g}	ϕ_3	-.57734	-.28546	-.29188	.57734	.28546	-.29188
	E _{2u}	ϕ_4	.57735	-.28863	-.28872	.57735	-.28863	-.28872
	E _{2u}	ϕ_5	.00005	-.50002	.49998	.00005	-.50002	.49998
	B _{2g}	ϕ_6	-.40825	.40825	-.40825	.40825	-.40825	.40825
15°	A ₁	ϕ_1	.40398	.41036	.41036	.40398	.41036	.41036
	B ₁	ϕ_2	.00000	-.50000	-.50000	.00000	.50000	.50000
	B ₂	ϕ_3	-.58034	-.28566	.28566	.58034	.28566	-.28566
	A ₁	ϕ_4	.58034	-.28566	-.28566	.58034	-.28566	-.28566
	A ₂	ϕ_5	.00000	-.50000	.50000	.00000	-.50000	.50000
	B ₂	ϕ_6	-.40398	.41036	-.41036	.40398	-.41036	.41036
22.5°	A ₁	ϕ_1	.39823	.41316	.41316	.39823	.41316	.41316
	B ₁	ϕ_2	.00000	-.50000	-.50000	.00000	.50000	.50000
	B ₂	ϕ_3	-.58430	-.28159	.28159	.58430	.28159	-.28159
	A ₁	ϕ_4	.58430	-.28159	-.28159	.58430	-.28159	-.28159
	A ₂	ϕ_5	.00000	-.50000	.50000	.00000	-.50000	.50000
	B ₂	ϕ_6	-.39823	.41316	-.41316	.39823	-.41316	.41316
30°	A ₁	ϕ_1	.38991	.41712	.41712	.38991	.41712	.41712
	B ₁	ϕ_2	.00000	-.50000	-.50000	.00000	.50000	.50000
	B ₂	ϕ_3	-.58989	-.27570	.27570	.58989	.27570	-.27570
	A ₁	ϕ_4	.58989	-.27570	-.27570	.58989	-.27570	-.27570
	A ₂	ϕ_5	.00000	-.50000	.50000	.00000	-.50000	.50000
	B ₂	ϕ_6	-.38991	.41712	-.41712	.38991	-.41712	.41712

TABLE III

ELECTRONIC CONFIGURATIONS (SINGLY EXCITED) AND THEIR ENERGIES AND SYMMETRIES FOR BENZENE AND BENT BENZENE

ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6	Symmetry			Configuration energy, e.v.			
						Benzene	Bent benzene	Configura- tion	0°	15°	22.5°	30°
2	2	2				¹ A _{1g}	A ₁	V ₀	-80.023	-79.474	-78.795	-77.922
2	2	1	1			¹ E _{1u}	B ₂	V ₃₄	-73.680	-73.450	-73.134	-72.729
2	2	1		1		¹ E _{1u}	B ₁	V ₃₅	-74.281	-73.887	-73.395	-72.764
2	2	1			1	¹ E _{2g}	A ₁	V ₃₆	-71.594	-71.357	-71.033	-70.619
2	1	2	1			¹ B _{2u}	B ₁	V ₂₄	-74.281	-73.887	-73.395	-72.764
2	1	2		1		¹ B _{1u}	B ₂	V ₂₅	-73.680	-73.084	-72.377	-71.466
2	1	2			1	¹ E _{2g}	A ₂	V ₂₆	-71.594	-71.161	-70.639	-69.967
1	2	2	1			¹ E _{2g}	A ₁	V ₁₄	-71.594	-71.357	-71.033	-70.619
1	2	2		1		¹ E _{2g}	A ₂	V ₁₅	-71.594	-71.161	-70.639	-69.967
1	2	2			1	¹ B _{1u}	B ₂	V ₁₆	-68.492	-68.237	-67.924	-67.524

TABLE IV

CONFIGURATION INTERACTION MATRIX ELEMENTS (E.V.) FOR BENZENE AND BENT BENZENE

Interaction	0°	15°	22.5°	30°
$\langle V_0 V_{36} \rangle$	0.000	-0.012	-0.011	-0.014
$\langle V_0 V_{14} \rangle$.000	.012	.011	.014
$\langle V_{26} V_{15} \rangle$	-.099	-.103	-.106	-.108
$\langle V_{26} V_{14} \rangle$	-.099	-.074	-.041	.005
$\langle V_{34} V_{14} \rangle$	-.067	-.068	-.088	-.118
$\langle V_{34} V_{25} \rangle$	-.353	-.354	-.373	-.399
$\langle V_{16} V_{26} \rangle$	-.068	-.050	-.033	-.007
$\langle V_{24} V_{36} \rangle$.954	.936	.911	.874
$\langle V_{25} V_{35} \rangle$	-.004	.000	.000	.000
$\langle V_{26} V_{14} \rangle$.000	.000	.000	.000
$\langle V_{35} V_{34} \rangle$	-.015	.000	.000	.000
$\langle V_{35} V_{16} \rangle$.000	.000	.000	.000
$\langle V_{34} V_{24} \rangle$	-.004	.000	.000	.000
$\langle V_{16} V_{24} \rangle$.000	.000	.000	.000
$\langle V_{26} V_{14} \rangle$	-.001	.000	.000	.000
$\langle V_{26} V_{36} \rangle$.000	.000	.000	.000
$\langle V_{16} V_{14} \rangle$	-.004	.000	.000	.000
$\langle V_{16} V_{36} \rangle$.001	.000	.000	.000

programs.²⁰ The molecular integrals are also given in Table I. A configuration interaction treatment using

(20) R. B. Hermann, *J. Org. Chem.*, **27**, 441 (1962). Most of the required equations are given in a paper by R. Pariser, *J. Chem. Phys.*, **24**, 250 (1956). Unfortunately these equations contain a number of typographical errors which were corrected by Dr. Pariser in a private communication to the

all singly excited configurations was carried out. The configuration energies are given in Table III and the configuration interaction matrix elements used are given in Table IV. Diagonalization²¹ of the elements gave the energy levels in Table V.

Goeppert-Mayer and Sklar have discussed the electronic transitions in benzene,¹³ where the molecular orbitals are completely determined by symmetry. The energy levels of the molecular orbitals are illustrated in Fig. 1. The ³B_{1u} triplet state of energy T₃₄

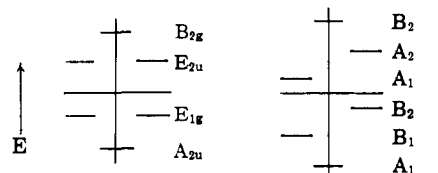


Fig. 1.—Schematic representation of the energy levels of benzene: D_{6h} on the left, C_{2v} on the right.

was found by subtracting 2K₃₄ from V₂₄. The four lowest transition energies obtained are in excellent agreement with experiment (Table VI).

authors. The computer programs were written to solve these corrected equations.

(21) The matrices were diagonalized by the Jacobi rotation method, discussed in H. H. Harmon, "Modern Factor Analysis," University of Chicago Press, Chicago, Ill., 1960, p. 180.

TABLE V
 STATE ENERGIES AND TRANSITIONS ABOVE THE GROUND STATE FOR BENZENE AND BENT BENZENE (E.V.)

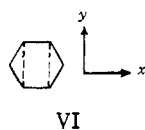
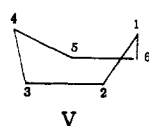
Symmetry			State energies				Transition energies			
Benzene	Bent benzene	State ^a	0°	15°	22.5°	30°	0°	15°	22.5°	30°
¹ A _{1g}	A ₁	V ₀	-80.023	-79.474	-78.795	-77.922	0.00	0.00	0.00	0.00
¹ B _{1u}	B ₂	V ₃₄	-74.034	-73.666	-73.289	-72.847	5.99	5.81	5.51	5.08
¹ E _{1u}	B ₁	V ₃₅	-73.338	-72.951	-72.484	-71.890	6.70	6.52	6.31	6.03
¹ E _{2g}	A ₁	V ₃₆	-71.497	-71.432	-71.074	-70.614	8.53	8.04	7.72	7.31
¹ B _{2u}	B ₁	V ₂₄	-75.235	-74.823	-74.306	-73.638	4.79	4.65	4.49	4.28
¹ E _{1u}	B ₂	V ₂₅	-73.316	-72.868	-72.224	-71.351	6.70	6.61	6.57	6.57
¹ E _{2g}	A ₂	V ₂₆	-71.695	-71.264	-70.744	-70.075	8.33	8.21	8.05	7.85
¹ E _{2g}	A ₁	V ₁₄	-71.691	-71.283	-70.992	-70.624	8.33	8.19	7.80	7.30
¹ E _{2g}	A ₂	V ₁₅	-71.493	-71.059	-70.534	-69.859	8.53	8.42	8.26	8.06
¹ B _{1u}	B ₂	V ₁₆	-68.490	-68.235	-67.922	-67.521	11.53	11.24	10.87	10.40

^a The symbols here are used to indicate states rather than configurations.

 TABLE VI
 TRANSITION ENERGIES IN BENZENE (E.V.)

Transition	Experimental ¹⁴	Calculated
¹ B _{2u} (forbidden)	4.71	4.79
¹ B _{1u} (forbidden)	5.96	5.99
¹ E _{1u} (allowed)	6.76	6.70
³ B _{1u} (forbidden)	3.59	3.59

The distortion of the benzene ring from the regular D_{6h} symmetry to a boat-like shape C_{2v} as must exist in the paracyclophanes may now be considered. Since the ¹E_{1u} level is doubly degenerate it can be anticipated that it may split as the ring is bent, and the bands can



all be expected to shift. The magnitude of the splitting and shifting is dependent on the degree of bending, and the latter is not yet known for the actual compounds. The approach therefore has been to calculate the spectrum for various degrees of bending, and to compare the calculated and observed spectra. Such a comparison should allow the degree of bending to be estimated for the various known cyclophanes, and a prediction of the electronic spectrum of the as yet unknown [7]paracyclophane can be made.

Transitions between the two pairs of doubly degenerate molecular orbitals of D_{6h} benzene were considered by Goepfert-Mayer and Sklar. When an electron is moved from an E_{1g} orbital to an E_{2u} orbital, two states of symmetry B_{1u} and B_{2u} and a doubly degenerate state of symmetry E_{1u} are obtained. In the group D_{6h} the electric dipole moment vectors M_x and M_y transform like E_{1u}, and M_z transforms like A_{2u}.

$$E_{1g} \times E_{2u} = B_{1u} + B_{2u} + E_{1u}$$

Therefore, of the singlet transitions from the closed shell ground state, A_{1g}, to these three upper states, two are forbidden transitions and one is an allowed transition (Table VI). The non-planar benzene found in [8]paracyclophane belongs to the group C_{2v}. As shown in Fig. 1, the molecular orbitals that were degenerate in benzene are not degenerate here. If these molecular orbitals are considered in an analogous way the following upper states are found

$$\begin{aligned} B_1 \times A_1 &= B_1 \\ B_1 \times A_2 &= B_2 \\ B_2 \times A_1 &= B_2 \\ B_2 \times A_2 &= B_1 \end{aligned}$$

In C_{2v} the electric dipole moment vector M_x transforms like B₁, M_y transforms like B₂ and M_z like A₁ (VI).

Transitions to these four upper states from the closed shell A₁ ground state are all allowed and have the symmetries

$$A_1 \times B_1 = B_1; A_1 \times B_2 = B_2; A_1 \times B_2 = B_2; A_1 \times B_1 = B_1$$

A benzene molecule was then considered in which atoms 1 and 4 were moved up out of the plane of atoms 2, 3, 5 and 6 (V). The angle θ is the angle between the planes defined by atoms 2, 3, 5 and 6; and 1, 2 and 6. The calculations were carried out for $\theta = 15^\circ$, 22.5° and 30° , as the [8]- and [7]paracyclophanes are probably in this range. Angles 345 and 216 were maintained at 120° throughout.

It was assumed that σ - π interaction was negligible for the non-planar system, and only the π -component was considered. The bond lengths do not remain equal when the ring is bent, so these were first calculated for $\theta = 30^\circ$. A Hückel matrix for the molecule was constructed using the matrix elements $\alpha = 0$ and $\beta_{12} = 0.85\beta_{23}$. From the bond orders p_{pq} , bond lengths were calculated and using eq. 5²² (where S is the pure single bond length, D is the pure double bond

$$r_{pq} = S - \{(S - D)/[1 + 0.765\{(1 - p_{pq})/p_{pq}\}]\} \quad (5)$$

length, and r is the distance corresponding to bond order p).²³ The bond lengths were $r_{12} = 1.400 \text{ \AA}$, $r_{23} = 1.392 \text{ \AA}$. and were found to be self-consistent. For $\theta = 22.5^\circ$ and $\theta = 15^\circ$, these values were modified by assuming the change in bond length was proportional to θ . The angles between the p orbitals at C-1 and C-2 were $17^\circ 11'$, $25^\circ 33'$ and $33^\circ 41'$ for $\theta = 15$, 22.5 and 30° , respectively. In finding the two-electron repulsion integrals between atoms, only the distances r_{ab} were considered and the orbitals were assumed to be parallel.

Resonance integrals between non-nearest neighbors were taken as zero, and those between nearest neighbors were found from eq. 2. In the case of the non-parallel orbitals, the value from 2 was multiplied by the cosine of the angle of deviation. Alpha was calculated neglecting penetration integrals.

The data necessary for construction of the H_{core} and Γ -matrices are given in Table I.

The calculated electronic spectra of benzene for various values of θ are given in Table V.

To obtain calculated values which can be compared to experiment it must be noted that the values in Table V are for benzene itself, while the actual compounds being examined are *p*-dialkylbenzenes. The effect of the side chains must now be taken into account. This can be conveniently done by a simple empirical procedure that will also take into account the fact that the experimental values are, for other than benzene itself, not the 0-0 transitions, but simply correspond to the wave length of the center of gravity of the band.

(22) C. A. Coulson, *Proc. Roy. Soc. (London)*, **A169**, 413 (1939).

(23) Here S and D are taken as 1.54 and 1.34 \AA , respectively.

TABLE VII
CALCULATED TRANSITION ENERGIES FOR *p*-DIALKYL BENZENES
(E.V.)

	0°	15°	22.5°	30°
	4.68	4.54	4.38	4.17
	5.79	5.61	5.34	4.91
	6.44	6.26	6.05	5.77
	6.44	6.35	6.31	6.31
	8.13	7.92	7.56	7.10

TABLE VIII
THE PREDICTED ULTRAVIOLET SPECTRA OF THE *p*-CYCLOPHANES

log ϵ	0°	15°	22.5°	30°
2	264	273	283	297
4	212	221	233	254
5	193	198	205	215
5	193	195	196	196
..	152	157	164	175

TABLE IX
THE OBSERVED ULTRAVIOLET SPECTRA OF THE [*m*]PARACYCLOPHANES

Compound	λ_{\max} (log ϵ)			
<i>p</i> -Diethylbenzene	193(4)	193(4)	214(3)	265(2)
[12]Paracyclophane ^a	220(3)	267(2)
[10]Paracyclophane ^a	223(3)	268(2)
[9]Paracyclophane	..	198(4)	224(3)	271(2)
[8]Paracyclophane	<200(4)	205(4)	230(3)	275(2)
[7]Paracyclophane (predicted)	196(4)	210(4)	247(3)	288(2)

^a These values are from ref. 4a; the other values were measured in the present work.

In *p*-diethylbenzene there are seen three absorption bands at 265, 214 and 193 $m\mu$, which correspond to energies of 4.68, 5.79 and 6.44 e.v. For D_{6h} benzene the corresponding calculated values are 4.79, 5.99 and 6.70 e.v. In each case therefore the actual energy of the transition is lower than that calculated by 0.1 to 0.3 e.v., for the reasons discussed. The easiest approximation now is to assume that the same differences will hold in the C_{2v} cases. When these side chain corrections are added to the values in Table V (0.2 e.v. is added to the ${}^1E_{2g}$ transition arbitrarily) the calculated electronic spectra in the *p*-dialkylbenzene series are as given in Table VII.

In *p*-diethylbenzene itself the 6.44 band is intense (log ϵ 5), the 5.79 band is of moderate intensity (log ϵ 4), and the 4.68 band is weak (log ϵ 2). These intensities should be roughly maintained as the ring is bent. The predicted spectrum as a function of bending is as given in Table VIII.

The ring in the open chain compound has $\theta = 0$, and the [10]- and [12]paracyclophanes have θ about 5°. For [9], θ is about 15° and [8] is near 20°. Models suggest that [7]paracyclophane, if it can be prepared, should have θ near 25°. The spectrum predicted for this compound is one which has lost the vibrational fine structure²⁴ and consists of four peaks above 190 $m\mu$ as indicated in Table VIII. The ${}^1E_{2g}$ transition in benzene is predicted to occur at very short wave length (152 $m\mu$) and is masked by Rydberg transitions.²⁵ In the bent systems the band should approach the accessible region.

The observed ultraviolet spectra of the *p*-cyclophanes are as in Table IX.

The energy of the ground state as a function of the bending of the ring is also of interest. If it is assumed that the bending and compression energy changes involved for these systems are small relative to the

change in π -energy,²⁶ the total deformation energy of the molecule can be approximated by the change in π -energy with bending. For $\theta = 15^\circ$, 22.5° and 30° , these deformation energies are 0.55, 1.23 and 2.10 e.v., respectively. These energies should be easily detectable from heats of combustion. The deformation energy should be small for the [10]- and [12]paracyclophanes, but should amount to about 15 kcal./mole for the [9]-, 25 kcal./mole for the [8] and perhaps 35 kcal./mole for the [7]. With regard to strain energy, the [9], [8]- and [7]paracyclophanes should be roughly comparable to cyclooctane, cyclobutane and cyclopropane, respectively. The synthesis of [7]paracyclophane therefore seems feasible and has been undertaken.

It has been suggested²⁷ that 1,2,4,5-tetra-*tert*-butylbenzene is distorted into the form of a boat. The shifts reported in the ultraviolet spectrum relative to an appropriate model (planar or nearly so) amount to about 5, 9 and 5 $m\mu$. These shifts are similar to those found in [9]paracyclophane and indicate a deformation having θ about 15°, which should yield a loss of resonance energy of some 15 kcal./mole. The experimental heat of combustion gave an approximate value for the total strain energy as near 30 kcal./mole. While this strain energy, and those calculated in the present work, are all very rough, the agreement is quite satisfactory.

Experimental²⁸

4,5-Diketo-[9]paracyclophane was prepared as previously described⁹; m.p. 56–58° (reported⁹ m.p. 57.1–58.5°).

Monohydrazone of 4,5-Diketo-[9]paracyclophane (II).—To a mixture of 100 mg. (0.434 mmole) of I and 5 ml. of *p*-dioxane was added 19 mg. (0.594 mmole) of 95% anhydrous hydrazine. The mixture was heated at 100° in an oil-bath for 12 hours to give a solution of the crude monohydrazone of I. Evaporation of a small portion of this solution gave crude white crystals, m.p. 80–100° (literature⁹ m.p. 148°).

α -Diazoketone (III).—The *p*-dioxane solution of crude monohydrazone was dissolved in 25 ml. of diethyl ether. Then, employing the manganese dioxide oxidation procedure,¹⁰ 1.0 g. (0.0012 mole) of activated manganese dioxide²⁹ was added followed by about 0.1 g. of crushed potassium hydroxide pellets. The mixture was stirred at 25° for 2 hours. A small portion of the reaction mixture was removed, and the solvent was evaporated. The residue, m.p. 70–80°, had infrared absorption bands at 2030 and 1640 cm^{-1} characteristic of an α -diazoketone.³⁰ No bands were observable from 2000 to 1690 cm^{-1} . The remaining mixture was filtered to remove solids. The diethyl ether was distilled to give a solution of diazoketone III in about 5 ml. of *p*-dioxane.

4-Carboxy-[8]paracyclophane (IV).—The Wolff rearrangement was carried out in a manner analogous to the procedure used by Meinwald and Gassman.³⁰ To the *p*-dioxane solution of the α -diazoketone was added 1.5 ml. of water. The solution in a Pyrex flask was heated at 100° in an oil-bath for 5 hours while being irradiated with a 250-watt Sylvania sun lamp. After this time no α -diazo ketone was observable by infrared. The solution was transferred to a separatory funnel and 30 ml. of diethyl ether was added. The mixture was extracted three times with 10-ml. portions of 10% sodium hydroxide solution. The combined sodium hydroxide extracts were acidified with 6 *N* hydrochloric acid, and the acidified solution was extracted with diethyl ether. The diethyl ether extracts were dried and were evaporated to give 37.3 mg. of crude IV, m.p. 65–70°. Two recrystallizations from ethanol and water gave 25 mg. (25% based on I used) of IV, m.p. 80–81°.

Anal. Calcd. for $C_{16}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.53; H, 8.85.

The infrared spectrum of IV showed bands at 3300(*m*), 2740(*w*), 2560(*w*) and 1703(*s*) cm^{-1} characteristic of carboxylic acids; ultraviolet absorption: λ_{\max}^{EtOH} 230 $m\mu$, ϵ 7,480; λ_{\max}^{EtOH} 270 $m\mu$, ϵ 268;

(26) This assumption is probably not correct but at least allows a rough estimate of the strain energy to be made.

(27) C. Hoogzand and W. Hübel, *Tetrahedron Letters*, 637 (1961).

(28) The elemental analyses were performed by Dr. Alfred Bernhardt, Microanalytical Laboratory, Max Planck Institute, Mulheim (Ruhr), Germany. The infrared spectra were recorded with a Beckman model IR-4 spectrophotometer. The ultraviolet spectra were determined on a Cary model 14 spectrophotometer. All melting points were taken on a hot-stage and were uncorrected.

(29) J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen and T. Walker, *J. Chem. Soc.*, 1094 (1952).

(24) L. L. Ingraham, *J. Chem. Phys.*, **27**, 1228 (1957).

(25) P. G. Wilkinson, *Can. J. Phys.*, **34**, 596 (1956).

$\lambda_{\text{max}}^{\text{EtOH}}$ 276 m μ , ϵ 343; $\lambda_{\text{max}}^{\text{EtOH}}$ 283 m μ , ϵ 295. The n.m.r. spectrum in carbon tetrachloride with internal tetramethylsilane showed peaks at -1.70τ (COOH) + 2.95τ (ArH) and a poorly defined series of four peaks with areas approximately: 7.15τ (3), 7.62τ (2), 8.50τ (8), 9.35τ (4).

The *p*-bromoanilide of IV was prepared by conventional procedures³⁰; m.p. 199–200°.

(30) R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 200.

Anal. Calcd. for C₂₁H₂₄ONBr: Br, 20.68. Found: Br, 20.85.

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[CONTRIBUTION FROM THE MCPHERSON CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY, COLUMBUS 10, OHIO]

Synthesis and Properties of Highly Hindered Aliphatic Acids¹

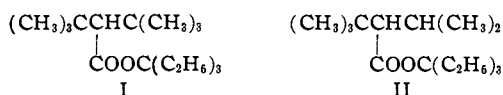
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The synthesis of several highly hindered aliphatic acids is described as well as certain reactions of these acids. The failure of triethylcarbinyl di-*tert*-butylacetate to react with amide ion provides an example of steric hindrance to proton removal. Ionization constants in 40% methanol at 40° for a number of hindered aliphatic acids have been determined and are listed in Table I.

In previous studies from this Laboratory, the syntheses of highly sterically hindered acids by alkylation of nitriles followed by hydrolysis of these nitriles have been described.³ When the degree of hindrance became too great, hydrolysis of nitriles to amides proceeded in such poor yield that this route to acids was poor.³ Accordingly, we were interested in finding out if the Hauser method⁴ of alkylation of triethylcarbinyl esters could be used in highly hindered cases.

Using this method we were able to prepare diisopropylmethylacetic, diisopropylethylacetic and triisopropylacetic acids from diisopropylacetic acid and *tert*-butylisopropylacetic acid from *tert*-butylacetic acid, but attempts to alkylate triethylcarbinyl di-*tert*-butylacetate (I) and triethylcarbinyl *tert*-butylisopropylacetate (II) failed, because of different reasons, as described below.



The failure to alkylate I using potassium amide and alkyl iodides in mixtures of ether and liquid ammonia is explained by the failure of amide ion to abstract the α -proton, as judged by the lack of any green color in the reaction mixture. This provides an example of steric inhibition of proton abstraction by an amide ion. In all cases (except one; see below) we have studied, a green color⁵ (undoubtedly due to enolate formation) was formed when successful alkylations resulted. The one exception was ester II, which under the usual conditions gave a yellow color. On the addition of isopropyl iodide this yellow color was discharged. However, the original ester II was recovered in 83% yield. Here the failure to alkylate may be explained by the competition of an elimination reaction involving isopropyl iodide. Thus, when the bulk of the anion becomes too great, elimination is favored over displacement.

Attempts to prepare anhydrides from highly hindered acids are of interest: for example, the behavior of di-

(1) This work was mainly supported by the United States Air Force under contract No. AF 33(616)-3412, monitored by the Aeronautical Research Laboratory, Wright Air Development Center.

(2) The material herein presented was taken from the Ph.D. Thesis, O.S.U., 1959, of T. F., who held a fellowship in 1956–1957 donated by the Research Corporation.

(3) L. Tsai, T. Miwa and M. S. Newman, *J. Am. Chem. Soc.*, **79**, 2530 (1957).

(4) C. R. Hauser and W. J. Chambers, *ibid.*, **78**, 3837 (1956).

(5) In ref. 4 above, the formation of a green color is also mentioned.

isopropylacetic acid and triisopropylacetic acid with ethoxyacetylene. The former acid, on refluxing with excess ethoxyacetylene in ether for one hour, yielded the anhydride in 39% yield, whereas the latter under similar conditions afforded a 61% yield of anhydride after five days. Thus, highly sterically hindered acids can be converted into their anhydrides by means of ethoxyacetylene but require much more drastic conditions than unhindered acids.⁶ The present examples provide other cases in which reactions involving cyclic mechanisms proceed in spite of a large amount of steric hindrance.⁷

In one attempt to prepare triisopropylacetic anhydride from the acid using trifluoroacetic anhydride⁸ the reaction failed because of evolution of carbon monoxide, even at 0°. The evolution of carbon monoxide is an indication that this reaction involves an oxocarbenium ion,⁹ formed by dissociation of the mixed anhydride into trifluoroacetate anion and triisopropylmethyl oxocarbenium ion.

In this connection the facile reaction of triisopropylacetyl chloride with methanol to afford methyl triisopropylacetate in 90% yield is of interest. Because of the ease of reaction one would surely rule out a carbonyl-addition mechanism on the basis of steric hindrance. Undoubtedly, then, the reaction involves ionization of the acid chloride to an oxocarbenium ion which reacts with methanol more rapidly than it decarbonylates. Gas evolution during the reaction period (in which the temperature rapidly rose from 0° to 40–50°) was not observed. When one recalls that a solution of triisopropylacetic acid in trifluoroacetic anhydride at 0° evolves carbon monoxide, the failure of the triisopropylmethyl oxocarbenium ion to lose carbon monoxide in methanol at 40–50° is noteworthy. Either the carbonium ion is stabilized by methanol as solvent before reaction to yield ester or the reaction of the carbonium ion with methanol is much faster than its cleavage to carbon monoxide and other products

(6) For the mechanism of anhydride formation see G. Eglinton, E. R. H. Jones, B. I. Shaw and M. C. Whiting, *J. Chem. Soc.*, 1860 (1954), and H. H. Wasserman and P. S. Wharton, *J. Am. Chem. Soc.*, **82**, 1411 (1960).

(7) R. H. Dewolfe and W. G. Young, *Chem. Rev.*, **56**, 875 (1956), show that allylmagnesium bromide adds to the highly hindered carbonyl group in certain mesityl ketones.

(8) E. J. Bourne, M. Stacey, J. C. Tatlow and R. Worrall, *J. Chem. Soc.*, 2006 (1954).

(9) (a) C. Schuerch, Jr., and E. H. Huntress, *J. Am. Chem. Soc.*, **71**, 2233 (1949), footnotes 13 and 14; (b) H. A. Smith and R. J. Smith, *ibid.*, **70**, 2400 (1948); (c) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 283.