paracyclophane of 13.2, and the other a molar ratio of 0.153. With both solutions, the two maxima occurred at the same wave lengths and with the same relative intensities, and the curve shapes were the same. Similar results were obtained with solutions of TCNE and [4.4]paracyclophane in which the molar ratios were varied from 15.3 to 0.220, and with solutions of TCNE and [6.6]paracyclophane in which the molar ratios were varied from 18.8 to 0.155. Solutions of all of the solid complexes in dichloromethane also gave maxima at the same wave length and at the same relative intensities for the two absorption bands as were observed for solutions made directly from the two components.

In a second set of experiments, the intensities of absorption at λ_{max} were demonstrated to be approximately the same for two solutions, one of which contained a two-to-one molar concentration of TCNE over paracyclophane, and the other of which contained a two-to-one molar concentration of paracyclophane over TCNE. The concentrations of the minor component in the two solutions were equal to one another. In the experiment with [2.2] paracyclophane and TCNE, the absorbance equalled 1.59 and 1.63 for the two solutions. In the experiment with [6.6]paracyclophane, the absorbance equalled 0.71 and 0.65 for the two solutions. This experiment demonstrates that the complex under observation is one-to-one.

TABLE V

RATIOS OF ABSORBANCE AT LONG AND SHORTER WAVE LENGTH MAXIMA OF PARACYCLOPHANE– AND MODEL–TCNE COMPLEXES IN DICHLOROMETHANE

π-Base	A_{LWLM}/A_{SWLM}[a]
[9]Paracyclophane	1.14
[10]Paracyclophane	1.09
[12]Paracyclophane	0.98
p-Xylene	.94
[1.7]Paracyclophane	.94
[1.8]Paracyclophane	.93
[1.9]Paracyclophane	.98
[1.10]Paracyclophane	.96
[1.11]Paracyclophane	.94
[1.12]Paracyclophane	.89
1,1-Bis-(4-*n*-propylphenyl)-methane	.82
[2.2]Paracyclophane	One peak
[2.3]Paracyclophane	One peak
[2.4]Paracyclophane	One peak
1,2-Bis-(4-ethylphenyl)-ethane	0.89
[3.3]Paracyclophane	1.08
[3.4]Paracyclophane	1.02
[3.6]Paracyclophane	0.93
1,3-Bis-(4-ethylphenyl)-propane	0.79
[4.4]Paracyclophane	1.05
[4.5]Paracyclophane	1.00
[4.6]Paracyclophane	.96
1,4-Bis-(4-ethylphenyl)-butane	.84
[5.5]Paracyclophane	.99
[5.6]Paracyclophane	.96
[6.6]Paracyclophane	.98
1,6-Bis-(4-*n*-propylphenyl)-hexane	.78

[a] A_{LWLM} = absorbance at λ_{max} of long wave length maxima, and A_{SMLM} = absorbance at λ_{max} of shorter wave length maxima.

In Table V is recorded the ratios of intensities of long wave length to shorter wave length maxima for the paracyclophane complexes and their models in dichloromethane. These ratios were independent of concentration of the complex in solution. The values of this ratio are highest in the most strained members of each series, and in general decrease as the strain is released.

Infrared Spectrum of [3.4]Paracyclophane–TCNE Complex.—The spectra of this complex, and of each component separately was taken on a Perkin–Elmer recording infrared spectrophotometer model 21 with sodium chloride optics and cells. The spectra were all determined in KBr pellets.

LOS ANGELES, CALIF.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES AND FROM THE ORGANISCH-CHEMISCHEN LABORATORIUM DER EIDG. TECHNISCHEN HOCHSCHULE]

Macro Rings. XXI. Mono- and Polysubstituted [2.2]Paracyclophanes[1]

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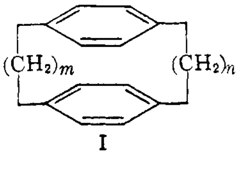
Nitration of [2.2]paracyclophane gave besides the mononitro derivative, two dinitro- compounds, one mononitro phenol and two dinitrophenols. Nitration of 4-acetamido[2.2]paracyclophane gave two mononitro derivatives. Structures for these compounds are suggested which depend on their physical and chemical properties. Attempts to introduce a second two-membered methylene bridge into [2.2]paracyclophane failed. The ultraviolet absorption spectra of substituted paracyclophanes are reported and discussed. The pK_a's of a number of paracyclophanecarboxylic acids and pK_b's of the corresponding amino compounds are reported.

Earlier studies demonstrated the presence in the smaller paracyclophanes of transannular effects in electrophilic substitution. The smaller the values of *m* and *n* in compounds of structure I, the faster the rate of introduction of the first acetyl group, and the slower the rate of introduction of the second.[2] In the preparation of disubstituted derivatives of [4.4]-[2d] and [6.6]paracyclophane,[2a] no transannular directive influences were observed.

The objectives of the present investigation were threefold: to determine if transannular directive effects govern the introduction of a second substituent into monosubstituted [2.2]paracyclophane; to correlate the ultraviolet spectra of the substituted paracyclophanes that have been prepared in these investigations; to correlate acid and base strengths of paracyclophanecarboxylic acids and amines with their structures.



I

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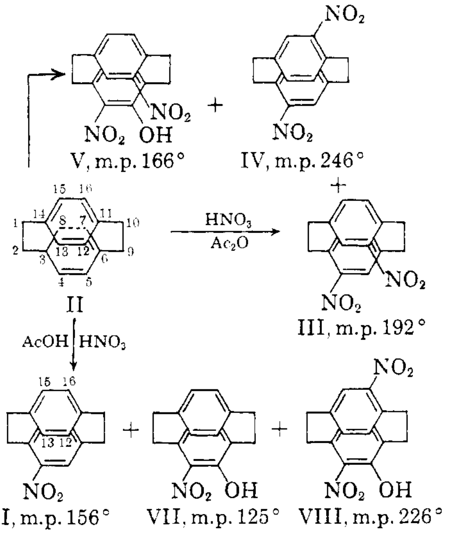
[1] The authors wish to thank the Upjohn Company for a generous research grant which supported this research.

[2] (a) D. J. Cram and J. Abell, THIS JOURNAL, **77**, 1179 (1955); (b) D. J. Cram and R. W. Kierstead, *ibid.*, **77**, 1186 (1955); (c) D. J. Cram and N. L. Allinger, *ibid.*, **77**, 6289 (1955); (d) D. J. Cram and R. A. Reeves, *ibid.*, **80**, 3094 (1958); (e) D. J. Cram, W. J. Wechter and R. W. Kierstead, *ibid.*, **80**, 3126 (1958).

Introduction of Two or More Substituents into [2.2]Paracyclophane.—Treatment of [2.2]paracyclophane (II) with a solution of fuming nitric acid in acetic anhydride gave a low yield of a mixture of two bis-nitro derivatives, whose structures are provisionally assigned as III and IV on the following grounds. In Table I is given the ultraviolet absorption maxima of the two isomers, of the mononitro compound, VI, and of model compounds. The spectra of compounds III and IV are very similar to one another. The spectra of nitrobenzene, *m*-dinitrobenzene and *p*-dinitrobenzene differ substantially from one another. These facts indicate that the two nitro groups of III and IV are in different rings. Had a second nitro group entered the substituted ring of VI, it could have occupied only the single unsubstituted *m*-position of the molecule.



V, m.p. 166°

IV, m.p. 246°

II

III, m.p. 192°

VI, m.p. 156°

VII, m.p. 125°

VIII, m.p. 226°

TABLE I

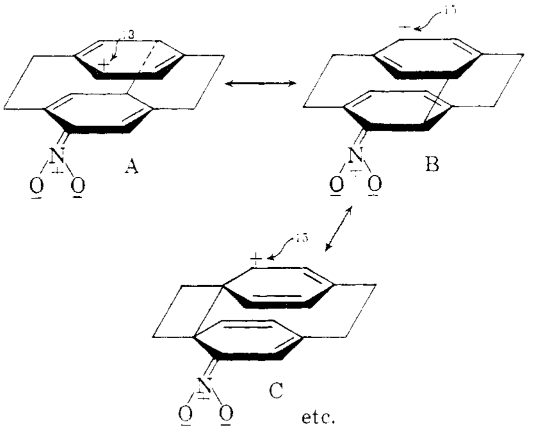
ULTRAVIOLET ABSORPTION MAXIMA OF NITRO[2.2]PARACYCLOPHANES AND MODEL COMPOUNDS

Compound	λ_{max}, mμ	ε
Nitrobenzene	269	7,800
	305 (sh)[a]	....
m-Dinitrobenzene	242	16,300
	305	1,100
p-Dinitrobenzene	266	14,500
[2.2]Paracyclophane	224	25,000
	284	250
	302	160
4-Nitro[2.2]paracyclophane (VI)	217	20,000
	304	7,000
Dinitro compound III	210	17,600
	294	3,800
Dinitro compound IV	210	19,300
	294	4,600

[a] Shoulder.

Thus one of the isomeric dinitro compounds would have had both nitro groups in the same ring, and in the other the two nitro groups would have been distributed in two different rings. Under such circumstances, the isomers would undoubtedly have had different ultraviolet spectra. The near identity of the infrared spectra of compounds VI,[2c] III and IV also supports the hypothesis that the two nitro groups of III and IV are in different rings. It also seems unlikely that the deactivating influence of a nitro group would be more felt in the unsubstituted than in the substituted ring of VI. In the diacetylation of [4.4]-[2a] and [6.6]paracyclophanes,[2d] the two acetyl groups entered two different rings. Moreover, the ultraviolet absorption spectra of these isomeric bis-derivatives are almost identical to one another.

Since the two rings of the [2.2]paracyclophanes cannot rotate with respect to one another,[2c] four dinitro[2.2]paracyclophanes with nitro groups in different rings can be drawn, with nitro groups substituted in the 4,12-, 4,13-, 4,15- and 4,16-positions (see II). Since only two disubstituted isomers were isolated (approximately equal amounts), the four open positions of the unsubstituted ring of VI would seem to be subject to transannular directive influences of the substituent already in the ring of VI. Position 13 of VI is subject to steric deactivation, whereas positions 13 and 15 are probably deactivated due to transannular withdrawal of electrons from these carbon atoms (see resonance structures A, B and C). Had the nitro group of VI deactivated the unsubstituted ring by a general field effect, three of the isomeric dinitro compounds might have been produced. Thus the two isomeric bis-nitro compounds probably possess structures III and IV. The higher-melting compound is tentatively assigned the more symmetrical structure IV (center of symmetry), and the lower-melting compound the less symmetrical structure (racemate). These melting point relationships are carried over to the corresponding bis-acetamido derivatives (unpublished results). Similar melting point relationships were found to apply to the isomeric diacetyl[4.4]paracyclophanes[2d] and diacetyl[6.6]paracyclophanes.[2a]



A third substance, a dinitrophenol V, was produced in the nitration reaction carried out in acetic anhydride. The structure of this compound is discussed below.

When the nitration of [2.2]paracyclophane was carried out in glacial acetic and fuming nitric acid, the mononitro derivative VI was the main product. Small amounts of a mononitrophenol VII and a trace of a dinitrophenol VIII were also produced.

In basic alcohol solution, compounds V, VII and VIII produced a deep orange color which was discharged on addition of acid. The positions of the absorption bands in the ultraviolet absorption spectra of V, VII, VIII and of *o*-, *m*- and *p*-nitrophenols[3] in acid and basic solution are recorded in Table II.

The fact that V, VII and VIII undergo such marked changes in spectra with changes in acidity and basicity of the medium indicates that the ring containing a hydroxyl also contains a nitro group. The long wave length band of VII undergoes a shift of 88 mμ as a proton is lost from the hydroxyl. The long wave length band of 4-hydroxy[2.2]paracyclophane undergoes a shift of only 20 mμ (see Table IV), whereas those of *o*- and *p*-nitrophenol undergo shifts of 65 and 85 mμ, respectively, In principle, the hydroxyl and nitro groups of VII could be *o*, *m* or *p* to one another. However, oxidations of nitrobenzene give only *o*- and *p*-substituted products, which makes a *m*-structure for VII unlikely.[4] Of the two remaining structures for VII, the *o*-structure is preferred on stereoelectronic grounds. Either radical or nucleophilic attack on the 4-nitro[2.2]paracyclophane probably involves a transition state in which the two benzene rings become tilted somewhat with respect to one another to accommodate the extra volume required for one of the carbon atoms to pass from sp^2 to sp^3 hybridization. Attack at the position *para* to the nitro group would push the two rings together on the side carrying the nitro group, whereas attack at the position *ortho* to the nitro group would push the two rings together on the unsubstituted side. The latter possible reaction course would seem to involve less strain.

TABLE II

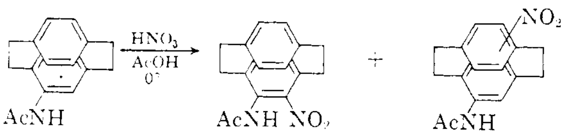
ULTRAVIOLET ABSORPTION MAXIMA OF NITROPHENOLS, [2.2]PARACYCLOPHANE AND MODEL COMPOUNDS

Compound	In acid[a] λ_{max}[c]	In acid[a] ε	In base[b] λ_{max}[c]	In base[b] ε
o-Nitrophenol[d]	209	14,800	228	16,000
	~230(sh)[e]	3,900	250	5,000
	279	6,600	282	4,300
	351	3,200	416	4,800
p-Nitrophenol[d]	226	6,900	226	6,500
	318	10,000	403	19,200
5-Hydroxy-4-nitro-[2.2]paracyclophane (VII)	~224(sh)[e]	16,700	~332(sh)[e]	26,000
	304	8,200	304	8,200
	372	4,020	460	8,900
4,12-Dinitro-5-hydroxy-[2.2]-paracyclophane (V)	~224(sh)[e]	18,000	~240(sh)[e]	18,400
	286	8,800	288	8,900
	352	3,950	452	5,600
4,16-Dinitro-5-hydroxy[2.2]-paracyclophane (VIII)	217	19,000	~223(sh)[e]	6,200
	312(sh)[e]	3,340	445	6,000
	344	3,500		

[a] Spectra taken in 0.1 *N* hydrogen chloride in ethanol. Spectra taken in 0.1 *N* sodium hydroxide in ethanol. [c] In mμ. [d] Taken from data of ref. 3. [e] Shoulder.

The structures provisionally assigned to compounds V and VIII are based on the probability that they are derived from III and IV, respectively, although other possibilities also exist. The similarity in the spectra of these compounds indicates that both substances must contain a hydroxyl and a nitro group in one ring (oriented in the same way with respect to one another), and a nitro group in the second ring which differs in its location in the two compounds. The higher-melting compound is assigned the more symmetrical structure.

Nitration of acetamido compound IX[2c] gave two mononitro derivatives, one of which is assigned structure X. The other compound probably possesses one of the structures that corresponds to XI.



IX X, m.p. 186° XI, m.p. 237°

A greater similarity exists in the ultraviolet absorption spectra of X and *o*-nitroacetanilide than in the spectra of X and *p*-nitroacetanilide (see Table III). The spectra of X and XI are quite different, and that of XI shows little resemblance to either of the model compounds.

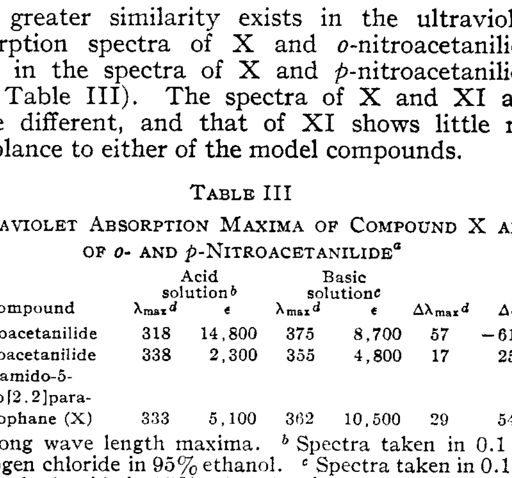
TABLE III

ULTRAVIOLET ABSORPTION MAXIMA OF COMPOUND X AND OF *o*- AND *p*-NITROACETANILIDE[a]

Compound	Acid solution[b] λ_{max}[d]	Acid solution[b] ε	Basic solution[c] λ_{max}[d]	Basic solution[c] ε	$\Delta\lambda_{max}$[d]	Δε
p-Nitroacetanilide	318	14,800	375	8,700	57	−6100
o-Nitroacetanilide	338	2,300	355	4,800	17	2500
4-Acetamido-5-nitro[2.2]paracyclophane (X)	333	5,100	362	10,500	29	5400

[a] Long wave length maxima. [b] Spectra taken in 0.1 *N* hydrogen chloride in 95% ethanol. [c] Spectra taken in 0.1 *N* sodium hydroxide in 95% ethanol. [d] In mμ.

Attempt to Introduce a Third Bridge into [2.2]-Paracyclophane.—Reactions are formulated which were designed to produce compound XIV. In practice, ketone XII[2c] was converted to XIII in poor yield, but the acid chloride of XIII failed to undergo ring closure. The distance between the 4- and 12-positions in this molecule are in excess of 3 Å.[5] Carbon atoms 3 and 6 are bent out of the plane of the other four, and as a result it seems probable that the carbon of the carbonyl group is below the plane occupied by carbons 4, 5, 7 and 8. Thus considerable strain would be involved in closing the third bridge to give XIV.



XII XIII XIV

Ultraviolet Absorption Spectra of the Paracyclophanes and Their Derivatives.—Evidence has accumulated that the abnormal ultraviolet absorption

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[3] L. Daub and J. Vandenbelt, THIS JOURNAL, **71**, 2414 (1949); **69**, 2714 (1947).

[4] J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 376 (1951).

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

spectra of the smaller paracyclophanes is due both to transannular electronic effects and to the lack of planarity of the benzene rings.[6] Through a study of the ultraviolet spectra of the one-to-one tetracyanoethylene complexes of the paracyclophanes, it was found[7] that in the [3.3]-compound the two benzene rings were an optimum distance from one another to allow a maximum electron release to the π-acid of the complex. This result suggests that bands might be present in the spectra of the paracyclophanes themselves which are relatively insensitive to the deformities of the benzene ring, and which reflect mainly transannular electronic effects. An examination of the spectra of the [*m.n*]paracyclophanes in which the benzene rings are parallel or nearly parallel to one another[6a] reveals that a band can be found in the spectra whose λ_{max} occurs at longest wave lengths when $m = n = 3$.

Table IV records the difference in wave length of the three major bands in the spectra of the paracyclophanes, and of those in the spectra of an open-chain model compound (*p,p'*-diethylbibenzyl). The band which occurs at 223 mμ in the model compound moves to its longest wave length in the [3.3]-compound, whereas the other two bands reach their longest wave length in the [2.2]-compound. The shifts in the band which occur at 265 mμ in the model compound drop off rapidly as the two rings of the paracyclophanes assume more natural configurations, whereas the shifts in the 273 mμ band of the model decrease much more slowly as the two rings get farther apart. These trends suggest that the shifts in the 223 mμ band are largely associated with transannular electronic effects, shifts in the 265 mμ band reflect mainly the deviations of the two benzene rings from their normal configurations, and that the shifts in the 273 mμ band are sensitive to both steric and electronic effects. These conclusions are in harmony with the interpretation which Ingraham[8] has given to the ultraviolet absorption spectrum of [2.2]-paracyclophane.

TABLE IV

DIFFERENCES IN THE ULTRAVIOLET ABSORPTION SPECTRA OF [*m.n*]PARACYCLOPHANES AND OF OPEN-CHAIN MODEL[a]

Compound $(p\text{-}C_2H_5C_6H_4CH_2)_2$	Absorption maxima of model in mμ		
	223	265	273
Paracyclophane	Δλ[b]	Δλ[b]	Δλ[b]
[6.6]-	2	1	1
[5.5]-	2	1	1
[4.4]-	3	1	1
[3.4]-	9	1	7
[3.3]-	23	4	21
[2.3]-	20	10	26
[2.2]-	21	21	29

[a] Ref. 2c. [b] In mμ.

Table V records the wave length and intensity of the absorption bands in the ultraviolet absorption spectra of monosubstituted paracyclophanes, and of their open-chain models. In Table VI is found the differences in wave length for the principal bands in the spectra of the cycles, and in the spectra of the models. In some cases it was difficult to identify the bands, both because of their overlap with adjacent bands, and because of the large differences in spectra between the open-chain models and the smaller of the paracyclophanes. In spite of these ambiguities, a number of trends in the data are visible: (1) Transannular effects as reflected in ultraviolet spectra start to assert themselves as the distance between the two benzene rings decreases to the point where $m = n = 4$. The spectral abnormalities in the mono-substituted [4.4]paracyclophanes are more pronounced than in [4.4]paracyclophane itself (see Table IV). (2) The longest wave length band of the monosubstituted [*m.n*]paracyclophanes increases regularly as the values of *m* and *n* decrease and the rings get closer together. The effect is least when the substituent is a nitro and most when the substituent is a carboxyl group. As with the paracyclophanes themselves, this effect probably reflects both the distortion of the benzene rings from their normal planar configurations in the lower homologs (particularly for $m = n = 2$), and the interaction of the π-electrons of the two rings with one another. (3) The same kind of trend is detectable in the absorption bands which occur in the middle region, but the results are more erratic. (4) The short wave length band absorbs at longer wave lengths in the [3.4]- than in the [2.2]paracyclophane, when the substituent is a nitro or carboxyl group. With the other groups, the band could not be detected in either the [2.2]- or the [3.4]-compound. The shorter wave length band of the hydrocarbons themselves reached a maximum with $m = n = 3$ (see Table IV), and seemed to be associated with mainly transannular electronic effects. The data suggest that a similar association applies to the shorter wave length band of the monosubstituted compounds.

Apparent pK_a's of Paracyclophane Acids and of the Conjugate Acids of the Corresponding Amino Compounds.—Table VII records the values of the apparent pK_a's of a number of paracyclophane-carboxylic acids and conjugate acids of paracyclophane amines. These values were determined in 80% methyl Cellosolve–20% water by a method previously described.[9] Compound XIX (Table VII), which contains only one benzene ring, serves as a model for the other monocarboxylic acids (XVII, XVIII, XX and XXI). Within the probable error (±0.07 *pK* unit), these values are the same, and therefore no field or resonance effect associated with the unsubstituted benzene ring is visible in these results. The relative stabilities of the acid and of its conjugate base are unaffected by the presence of the second ring, or by the deformation of the benzene ring of the smallest homolog from its normal planar configuration. The absence of these effects contrasts with those observed in electrophilic substitution, in which rates of acetylation varied by a factor of at least 50 in passing from [6.6]- to [2.2]paracyclophane.[2c]

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(6) (a) D. J. Cram, N. L. Allinger and H. Steinberg, THIS JOURNAL, **76**, 6132 (1954); (b) D. J. Cram and M. F. Antar, *ibid.*, **80**, 3105 (1958).

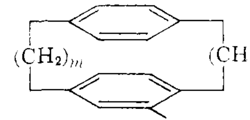
(7) D. J. Cram and R. H. Bauer, *ibid.*, **81**, 5971 (1959).

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

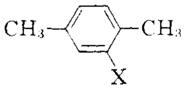
(9) (a) W. Simon, E. Kovats, L. H. Chopard-dit-Jean and E. Heilbronner, *Helv. Chim. Acta*, **37**, 1872 (1954); (b) W. Simon and E. Heilbronner, *ibid.*, **38**, 508 (1955); (c) W. Simon, D. Meuche and E. Heilbronner, *ibid.*, **39**, 290 (1956).

TABLE V

ABSORPTION BANDS IN THE ULTRAVIOLET SPECTRA OF MONOSUBSTITUTED PARACYCLOPHANES IN 95% ETHANOL



XV



XVI

General structure	m	n	X	Absorption maxima in mμ (log ϵ) Short	 Medium	 Long
XVI^{a}	..	..	NO$_2$	$\sim$205(4.24)^{b}	265(3.82)	$\sim$295(3.32)^{b}
XV^{c}	6	6	NO$_2$	.....^{d}	265(3.64)	$\sim$295(3.20)^{b}
XV^{c}	4	4	NO$_2$	.....^{d}	267(3.61) 274(3.59)	$\approx$300(3.0)^{b}
XV^{e}	3	4	NO$_2$	$\approx$230(3.8)^{b,d}	273(3.50) 280(3.50)	$\approx$305(3.0)^{b}
XV^{f}	2	2	NO$_2$	217(4.34)	$\approx$260(3.4)^{b}	307(3.47)
XVI^{a}	..	..	COCH$_3$	210(4.42)	250(3.95)	295(3.19)
XV^{g}	6	6	COCH$_3$	214(4.46)	250(3.86)	295(3.16)
XV^{c}	4	4	COCH$_3$	.....^{d}	253(3.83)	295(3.10)
XV^{e}	3	4	COCH$_3$	.....^{d}	257(3.44)	311(2.75)
XV^{f}	2	2	COCH$_3$	210(4.52)	$\approx$242(3.7)^{b} 286(3.58)	$\sim$328(2.9)^{b}
XVI^{a}	..	..	CO$_2$H	232(2.61)^{d} 260(2.69)^{h}	266(2.69)^{h} 269(2.81)^{h}	276(2.98)^{h} 286(2.91)
XV^{c}	4	4	CO$_2$H	$\approx$222(4.1)^{b,d} $\sim$235(3.75)^{b,d}	265(3.00)^{h} 268(2.99)^{h}	274(3.08)^{h} 288(3.11)
XV^{e}	3	4	CO$_2$H	$\approx$243(3.6)^{b,d}	273(3.11)	302(2.92)
XV^{f}	2	2	CO$_2$H	226(4.09)^{d}	276(3.47)	326(2.72)
XVI^{i}	..	..	OH	$\sim$218(3.87)^{b}	277(3.32)	......
XV^{i}	4	4	OH	$\sim$222(3.8)^{b}	275(3.26)	......
XV^{i}	2	2	OH	224(4.17) $\sim$244(3.5)^{b}	283(2.78) 290(2.87)	312(2.78) ......
XVI^{j}	..	..	O$^-$	243(3.91)	......	295(3.55)
XV^{j}	4	4	O$^-$	245(3.77)	275(3.26)	298(3.50)
XV^{j}	2	2	O$^-$	.......^{k}	284(3.08)	332(2.75)
XVI^{a}	..	..	NH$_2$	$\sim$220(3.8)^{b} 235(3.52)	260(2.68)^{h} 266(2.75)^{h} 269(2.81)^{h}	275(2.96)^{h} 298(3.00)
XV	4	4	NH$_2$	$\sim$221(4.0)^{b} $\sim$239(3.7)^{b}	268(3.03)^{h} 275(3.12)^{h}	289(3.23)
	3	4	NH$_2$	$\approx$250(3.6)^{b}	......	298(3.11)
	2	2	NH$_2$	$\sim$222(4.2)^{b}	272(3.41)	323(2.82)
XVI	2	2	NH$_3$$^+$	223(4.26)	$\sim$246(3.4)^{b} 286(2.41)	303(2.13)

[a] Mixed with an equal molar amount of *p*-xylene. [b] Inflection or shoulder. [c] Ref. 2d. [d] Spectra not taken below 220 mμ. [e] Ref. 2e. [f] Ref. 2c. [g] Ref. 2a. [h] Fine structure of *p*-xylene. [i] Ethanol, 0.1 *N* in HCl. [j] Ethanol, 0.1 *N* in KOH. [k] Spectra not taken below 240 mμ.

As might be expected,[9c] the pK_a's of the first carboxyls of the four dicarboxylic acids are lower than those of the monocarboxylic acids, and lowest for that compound in which the two carboxyl groups are closest together (XXIV). The pK_a's for the first carboxyls of the other three bis-acids (XXII, XXIII and XXV) are the same within probable error of one another. The ΔpK_a's of the four acids are small enough to suggest that the carboxyl groups are *trans* to one another.[9c] The identity of the values of ΔpK_a for the two [6.6]-bis-acids indicates that the distance between the two carboxyls in these compounds are comparable to one another on a time average basis. As expected, ΔpK_a for XXIV > ΔpK_a for XXV > ΔpK_a for XXII or XXIII. The fact that ΔpK_a is smaller for isomer XXV confirms the structures provisionally assigned to it and to XXIV earlier.[2d]

The pK_a's of the conjugate acids of the three amino-paracyclophanes differ from one another only by 0.33 pK_a unit. The *corresponding amines* can be arranged in the following order of their base strengths, [3.4] > [4.4] > [2.2]. The differences are small, and probably opposing forces (*e.g.*, steric and electronic) produce a leveling effect on these physical properties.[10]

Experimental

4,16-Dinitro[2.2]paracyclophane (IV), 4,12-Dinitro-[2.2]paracyclophane (III) and 5-Hydroxy-4,12-dinitro [2.2]-paracyclophane (V).—A solution of 1.0 g. of [2.2]paracyclophane in 100 ml. of boiling acetic anhydride was cooled to room temperature, and the solute separated. Fuming nitric

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[10] Opposing effects were observed to operate in controlling the relative abilities of the paracyclophanes to release electrons to the π-acid, tetracyanoethylene [D. J. Cram and R. H. Bauer, ref. 7].

TABLE VI

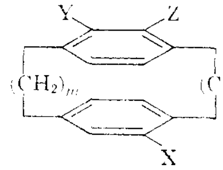
DIFFERENCES IN THE ULTRAVIOLET ABSORPTION SPECTRA OF X[*m.n*]PARACYCLOPHANES AND OF THE OPEN-CHAIN MODEL[a]

m	*n*	X	$\Delta\lambda^b$	$\Delta\lambda^b$	$\Delta\lambda^b$
6	6	NO_2	. .	0	~0
4	4	NO_2	. .	2 and 9	~5
3	4	NO_2	≈25	8 and 15	≈10
2	2	NO_2	~12	≈ −5	~12
6	6	$COCH_3$	4	0	0
4	4	$COCH_3$	. .	3	0
3	4	$COCH_3$	. .	7	16
2	2	$COCH_3$	−4	≈ −8 and 36	33
4	4	CO_2H	−10 and 3	. .	2
3	4	CO_2H	≈11	. .	16
2	2	CO_2H	−6	. .	40
4	4	OH	4	−2	. .
2	2	OH	6 and 26	6 and 13	. .
4	4	O^-	2	. .	3
2	2	O^-	. .	. .	37
4	4	NH_2	~1	~4	−9
3	4	NH_2	. .	≈15	0
2	2	NH_2	~1	37	25

[a] Data of Table V employed. [b] In mμ.

TABLE VII

APPARENT pK_a'S AND pK_b'S OF PARACYCLOPHANECARBOXYLIC ACIDS AND AMINO COMPOUNDS, RESPECTIVELY[a]



Compound	*m*	*n*	X	Y	Z	pK^a	
XVII[b]	6	6	CO_2H	H	H	7.50	
XVIII[c]	4	4	CO_2H	H	H	7.58	
XIX[d]	4	4	CO_2H	H	H	7.54[d]	
XX[e]	3	4	CO_2H	H	H	7.53	
XXI[f]	2	2	CO_2H	H	H	7.46	
XXII[b]	6	6	CO_2H	H	CO_2H	6.92 1st.	Δ = 1.06
XXII[b]	6	6	CO_2H	H	CO_2H	7.98 2nd.	
XXIII[b]	6	6	CO_2H	CO_2H	H	7.02 1st.	Δ = 1.06
XXIII[b]	6	6	CO_2H	CO_2H	H	8.08 2nd.	
XXIV[c]	4	4	CO_2H	H	CO_2H	6.68 1st.	Δ = 2.18
XXIV[c]	4	4	CO_2H	H	CO_2H	8.86 2nd.	
XXV[c]	4	4	CO_2H	CO_2H	H	7.04 1st.	Δ = 1.21
XXV[c]	4	4	CO_2H	CO_2H	H	8.25 2nd.	
XXVI[c]	4	4	$+NH_3$	H	H	3.71	
XXVII[e]	3	4	$+NH_3$	H	H	3.90	
XXVIII[f]	2	2	$+NH_3$	H	H	3.57	

[a] Determined in 80% methyl Cellosolve–20% water by weight. [b] Ref. 2a. [c] Ref. 2d. [d] In this compound, the unsubstituted aromatic ring was reduced to the hexahydroderivative, ref. 2b. [e] Ref. 2e. [f] Ref. 2c.

acid (9 ml.) was added very rapidly, and the resulting solution was poured through a sintered glass funnel into ice-water. About 30 seconds elapsed between the time the nitric acid was added and the time the solution was mixed with water. The tar-like mixture that separated was collected, dried, and triturated repeatedly with ether. The ether solution was evaporated to 25 ml. and chromatographed on 50 g. of activity II neutral alumina.[11] Ether (400 ml.) eluted a mixture of the two dinitro-compounds, which was rechromatographed as before, 50-ml. fractions being collected. Compound III was eluted with 300 ml. of 75% ether–pentane. When crystallized from ether, 0.050 g. of yellow material (III) was obtained, m.p. 191.5–192°.

Anal. Calcd. for $C_{16}H_{14}O_2N_4$: C, 64.43; H, 4.73. Found: C, 64.59; H, 4.69.

The next 250 ml. of 75% ether–pentane eluted compound IV, which when crystallized from ether gave 0.030 g. of yellow material, m.p. 246–247.5°. This compound was much more insoluble in organic solvents than its isomer.

Anal. Calcd. for $C_{16}H_{14}O_2N_4$: C, 64.43; H, 4.73. Found: C, 64.17; H, 4.57.

After compounds III and IV were eluted with ether from the first chromatogram, crude 5-hydroxy-4,12-dinitro[2.2]-paracyclophane (V) was eluted with 10% ethyl acetate–90% ether (300 ml.). The crude material was crystallized from ether and sublimed at 135° at 10^{-4} mm. The sublimate was washed with ether to give 0.015 g. of V, m.p. 166–166.5° (orange-yellow crystals).

Anal. Calcd. for $C_{16}H_{14}N_2O_5$: C, 61.15; H, 4.49. Found: C, 60.85; H, 4.16.

This substance when dissolved in a solution of sodium hydroxide in ethanol gave an intense orange color, which faded to a light yellow when the solution was acidified.

5-Hydroxy-4,16-dinitro[2.2]paracyclophane (VIII) and 5-Hydroxy-4-nitro[2.2]paracyclophane (VII).—These compounds were isolated as by-products of the mononitration of [2.2]paracyclophane.[2c] During the purification of 4-nitro [2.2]paracyclophane, a chromatogram was run, from which the monoderivative was eluted with ether–pentane.[2c] Elution of the column with methanol gave almost black material,[2c] which was rechromatographed in the present investigation on 50 g. of a one-to-one mixture of Celite and silicic acid. Elution of this column with pentane gave a solid material which was recrystallized from ether to give 0.010 g. of orange crystals, m.p. 206–209°. This material was sublimed at 135° and 10^{-4} mm., to give VIII as orange crystals, m.p. 226–228°.

Anal. Calcd. for $C_{16}H_{14}N_2O_5$: C, 61.15; H, 4.49. Found: C, 60.77; H, 4.67.

A sample of this material when dissolved in a solution of sodium hydroxide in ethanol gave an intense orange color which was discharged when the solution was acidified.

The mother liquor from the original crystallization of VIII was evaporated, and the residue was distilled at 170° and 10^{-4} mm. The distillate of oil and crystals was crystallized from ether to give 0.015 g. of orange-yellow crystals of VII, m.p. 125–126°.

Anal. Calcd. for $C_{16}H_{15}NO_3$: C, 71.35; H, 5.62. Found: C, 71.55; H, 5.64.

A sample of this material when dissolved in a solution of sodium hydroxide in ethanol gave an intense orange color which was discharged when the solution was acidified.

4-Nitro-5-acetamido[2.2]paracyclophane (X) and 4-Nitro-?-acetamido[2.2]paracyclophane (XI).—To a solution of 4 ml. of fuming nitric acid in 36 ml. of glacial acetic acid was added 0.46 g. of 4-acetamido[2.2]paracyclophane (IX)[2c] at room temperature. The reaction was allowed to proceed for 10 seconds (the red color of the mixture became slightly brown), and the solution was poured into a mixture of ice and water. The solid that separated was collected, dried, dissolved in ether and chromatographed on neutral, activity II alumina[11] (50 g.). The column was washed with 30% ether–pentane, and 50-ml. fractions of eluate were collected. Fractions 1 and 2 were essentially empty. Fractions 3 and 4 were combined, evaporated, and the residue was crystallized from a three-to-one methanol–water solution to give 0.040 g. of X, m.p. 186–188°.

Anal. Calcd. for $C_{18}H_{18}O_3N_2$: C, 69.67; H, 5.85. Found: C, 69.88; H, 6.02.

Fractions 5–8 were combined (0.12 g.) and chromatographed carefully with a procedure similar to that used the first time. Compound X was first eluted from the column, and the later fractions were rich in XI. These were combined and crystallized from methanol to give 0.010 g. of XI, m.p. 237–238°.

Anal. Calcd. for $C_{18}H_{18}O_3N_2$: C, 69.67; H, 5.85. Found: C, 69.25; H, 6.04.

4-Carboxymethylene[2.2]paracyclophane (XIII).—To a mixture of 0.5 g. of sulfur and 7 ml. of freshly distilled morpholine was added 1.0 g. of 4-acetyl[2.2]paracyclophane.[2c] The mixture was heated at reflux temperature for 15 hours, cooled, mixed with 20 ml. of 3 *N* hydrochloric acid, and the resulting mixture was extracted 3 times with ether. The ether extract was dried, evaporated, and the brown residue (thioacetomorpholide) was heated at reflux in 4 *N* ethanolic

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

sodium hydroxide for 15 hours. At the end of this time, the mixture was cooled, and stirred with 5 g. of Raney nickel. The mixture was filtered, evaporated, and the residue was sublimed at 0.4 mm. and 150°. The sublimate was crystallized from 95% ethanol to give 0.10 g. of the morpholide of XIII, m.p. 194–200°.

Anal. Calcd. for $C_{22}H_{25}O_2N$: C, 78.80; H, 7.52. Found: C, 79.10; H, 7.45.

In a second run, the above procedure was followed except that the thiomorphilide was hydrolyzed for 3 hours in 30 ml. of 4 *N* sodium hydroxide–ethylene glycol at reflux. The resulting mixture was cooled, and shaken with water and ether. The aqueous layer was acidified and extracted three times with ether. The ether extract was washed with water, dried, and evaporated to give a brown oil. This material was distilled at 170° and 10^{-4} mm. to give 0.10 g. of white crystals of acid XIII, m.p. 210–210.2°. An additional 0.070 g. of acid of similar melting point was recovered from the ether extract of the basic ethylene glycol solution.

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.08; H, 6.82.

Attempted Cyclization of 4-Carboxymethylene [2.2]paracyclophane (XIII), and Preparation of 4-Carboethoxymethylene[2.2]paracyclophane.—A solution of 0.085 g. of acid XIII in 3 ml. of thionyl chloride was held at reflux for 10 minutes, and the excess thionyl chloride was evaporated to give brownish crystals. This acid chloride was dissolved in a solution of 7 ml. of freshly-distilled *sym*-tetrachloroethane that contained 0.3 g. of anhydrous aluminum chloride. The mixture was swirled at room temperature for 5 minutes, cooled to 0° and diluted with 9 ml. of 1 *N* hydrochloric acid. The organic layer was separated, dried, and evaporated. The residue was chromatographed on 30 g. of activity II neutral alumina.[11] The column was washed with pentane to give only tetrachloroethane, and material was eluted with ether. The ether solution was evaporated, and the residue was crystallized from absolute ethanol to give crystals of ethyl ester of XIII, m.p. 79–79.8°, weight 0.020 g.

Anal. Calcd. for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.52; H, 7.72.

Ultraviolet Spectra.—The ultraviolet spectra were all taken in 95% ethanol in a Cary recording spectrophotometer, model 11PMS.

LOS ANGELES, CALIF.
ZURICH, SWITZ.

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

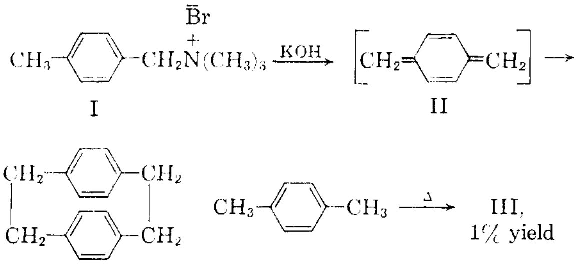
Macro Rings. XXII. Substituted Stilbenes from Attempted Dehydro[2.2]paracyclophane Synthesis[1]

BY DONALD J. CRAM AND RALPH H. BAUER

RECEIVED FEBRUARY 14, 1959

In an attempt to prepare 1,2-dehydro[2.2]paracyclophane (VI), 1,2-bis-(4-trimethylammoniummethylphenyl)-ethane dibromide (IV) was treated with base under a variety of conditions. The five stilbene derivatives VII, VIII, IX, X and XI were obtained.

When *p*-methylbenzyltrimethylammonium bromide (I) is treated with base, [2.2]paracyclophane (III) is produced.[2] The yields of III are much higher in this transformation than in the synthesis of III by the pyrolysis of *p*-xylene,[3] although both reactions presumably pass through *p*-xylylene (II)[4] as an intermediate. A similar reaction has been reported[5] in which 1,2-diphenyl[2.2]paracyclophane was prepared from *p*-benzylbenzyltrimethylammonium bromide.



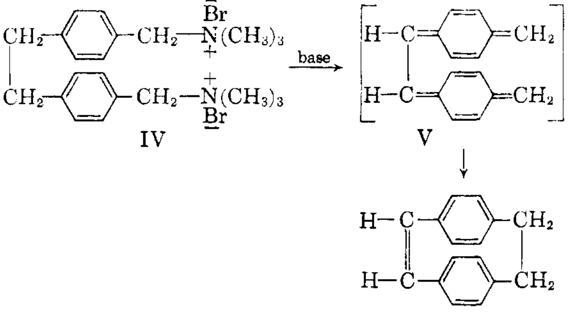
I

II

III, 20% yield

III, 1% yield

These results suggested that treatment of the bis-quaternary ammonium salt IV with base could lead to V, which might cyclize to give VI. This cycle has been previously prepared,[6] but the synthetic route was long and troublesome. Although attempts to convert IV to VI failed, products were encountered which are of interest because they appear to arise from intermediates that contain conjugated systems similar to that of II.



IV

V

VI

Elimination Reactions of Bis-quaternary Ammonium Salt IV.—When treated with sodium hydroxide under the Fawcett conditions[2] (aqueous solution at reflux), compound IV gave stilbene derivative VII. When the reaction was carried out in a refluxing solution of potassium hydroxide in di-

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[1] The authors wish to thank the Upjohn Co. for a generous research grant for the support of this research.

[2] [2.2]Paracyclophane has been prepared by extracting with toluene or with ethanol a polyparaxylylene obtained either by thermal decomposition of *p*-methylbenzyltrimethylammonium hydroxide (Fawcett, U. S. Patent 2,757,146, Ex. 1) or by the treatment of *p*-methylbenzyltrimethylammonium halide with concentrated aqueous alkali (British Patent 807,196, 1959). The details of these methods will shortly be published by Dr. H. E. Winberg and Dr. F. S. Fawcett of the Central Research Department, E. I. du Pont de Nemours and Co.

[3] C. J. Brown and H. C. Farthing, *Nature*, **164**, 915 (1949), and L. A. Errede, private communication.

[4] L. A. Errede and B. F. Landrum, THIS JOURNAL, **79**, 4952 (1957).

[5] H. W. Bersch, *Angew. Chem.*, **67**, 237 (1957).

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