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Macro Rings. XXVII. Transannular Substituent Effects in π - π -Complexes of Paracyclophanes¹

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The spectral properties of π - π -complexes between 13 monosubstituted [2.2]paracyclophanes and tetracyanoethylene have been examined. The position of λ_{\max} of the longest wave length charge transfer band in the ultraviolet spectrum of the complexes has been used as a measure of the relative π -base strengths of the substituted cycles. The method was checked through determination of the equilibrium constants of three of the one-to-one complexes. The expected correlation between the equilibrium constants and λ_{\max} was observed. For the electron-releasing groups, plots of the decrease in excitation energies due to the substituent against one particular set of σ^+ 's give a reasonably straight line for all except the hydroxyl and amino groups. These substituents themselves interact with tetracyanoethylene. Presumably the substituted ring is involved in these π - π -complexes. With electron-withdrawing groups, plots of the increase in excitation energy due to the substituent against σ_m and σ_p gave poor linear relationships. Of the two, σ_m 's provided the better. Presumably the non-substituted ring is directly involved in these complexes, and the substituent effects are of a transannular nature. The λ_{\max} of the tetracyanoethylene complex of [8]paracyclophane (benzene ring bent) was found to be identical with that of [9]- and [12]paracyclophanes (benzene rings not appreciably bent). The nuclear magnetic resonance spectra of the tetracyanoethylene complexes of [2.2]paracyclophane and of 4-ethyl[2.2]paracyclophane are indistinguishable from those of the parent hydrocarbons. The n.m.r. spectra of 8 of the monosubstituted paracyclophanes were determined. A bulk shift of all aromatic hydrogens was noted in going from electron-providing to electron withdrawing substituents. The fact that the hydrogens of the non-substituted ring also shifted provides evidence of transannular electronic effects.

Considerable evidence has accumulated for the presence of transannular electronic and steric effects in reactions and physical properties of the $[m.n]$ paracyclophanes.² This paper is concerned with the question of whether and how the electronic effects of substituents in one ring are transferred to the second ring of [2.2]paracyclophane.

Two techniques have been employed: (1) Others have demonstrated³ the existence of a correlation between the positions of λ_{\max} of the charge transfer bands of the ultraviolet spectra and the equilibrium constants for one-to-one complexes between tetracyanoethylene and ten methyl-substituted benzenes. In the present study, the λ_{\max} 's of the charge transfer bands of the π - π -complexes of tetracyanoethylene (TCNE) and thirteen monosubstituted paracyclophanes were measured, as well as the equilibrium constants for three of the complexes. With electron-providing substituents, the substituted ring was presumed mainly complexed, whereas with electron-withdrawing substituents the non-substituted ring was probably predominantly involved with TCNE. In the latter compounds, transannular substituent effects could be identified. In a subsidiary study, the effect of bending of a benzene ring on its π -base strength was assessed through determination of the position of λ_{\max} of the TCNE complex of [8]paracyclophane.

(2) Substituent effects on the chemical shift in the nuclear magnetic resonance (n.m.r.) spectra of the aromatic hydrogens in monosubstituted benzenes have been determined.⁴ A rough correlation between the magnitude of the chemical shift and the Hammett σ -substituent constants was noted. In the current investigation, the n.m.r. spectra of eight monosubstituted paracyclophanes were taken, and the magnitude

of the chemical shift of the aromatic hydrogens determined. The n.m.r. spectra of the TCNE complexes of [2.2]paracyclophane and 4-ethyl[2.2]paracyclophane were also taken and compared to those of the parent compounds.

Results

Starting Materials.—From previous investigations, 4-chloro-, 4-carboxy-, 4-amino-, 4-acetamido-, 4-hydroxy-, 4-acetyl- and 4-nitro[2.2]paracyclophane⁵ as well as [8]paracyclophane⁶ were available. Three additional substances, 4-bromo-, 4-methoxy- and 4-acetoxy[2.2]paracyclophane, were prepared in connection with another study, and their preparation and properties will be published in another paper.⁷ The remaining three compounds, 4-ethyl-, 4-cyano- and 4-carboxamido[2.2]paracyclophane were prepared by conventional reactions, the first from the 4-acetyl and the last two from the 4-carboxy compound (see Experimental).

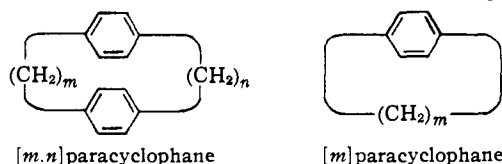
Equilibrium Constants.—The equilibrium constants of the 4-ethyl-, 4-acetyl- and 4-cyano[2.2]paracyclophane were measured at 25° in dichloromethane making use of the Benesi-Hildebrand equation (1).⁸ The method was previously applied to the TCNE complexes of the methylbenzenes.³ Good linear plots of $(A)l/(\log I_0/I)$ against $1/[D]$ were obtained for each of the

$$\frac{(A)l}{\log I_0/I} = \frac{1}{K\epsilon[D]} + \frac{1}{\epsilon} \quad (1)$$

where (A) = molar concentration of TCNE, l = cm. of light path, $[D]$ = mole fraction of the paracyclophane, ϵ is the apparent molar extinction coefficient and K is the equilibrium constant for the equation $\text{TCNE} + \text{paracyclophane} \rightleftharpoons \text{complex}$.

three compounds, which establishes that the complexes were indeed one-to-one. Table I records the K 's and ϵ 's for the complexes as well as those for *p*-xylene taken from the literature.³

Charge Transfer Bands of Complexes.—The charge-transfer spectra of the 13 complexes of the 4-substituted-[2.2]paracyclophanes and of [2.2]paracyclophane itself were determined at 25°. Table II records the results. The λ_{\max} 's were all obtained in dichloromethane containing equal molar concentrations of TCNE and π -base except in the case of the nitro compound, for



(1) The authors wish to thank the National Science Foundation for a grant used to support this investigation.

(2) (a) D. J. Cram, *Rec. Chem. Progr.*, **20**, 71 (1959); (b) D. J. Cram and D. I. Wilkinson, *J. Am. Chem. Soc.*, **82**, 5721 (1960); (c) D. J. Cram and L. A. Singer, *ibid.*, **85**, 1075 (1963).

(3) R. E. Merrifield and W. D. Phillips, *ibid.*, **80**, 2778 (1958).

(4) (a) P. L. Corio and B. P. Dailey, *ibid.*, **78**, 3043 (1956); (b) A. A. Bothner-By and R. E. Glick, *J. Chem. Phys.*, **26**, 1651 (1957).

(5) D. J. Cram and N. L. Allinger, *J. Am. Chem. Soc.*, **77**, 6289 (1955).

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

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TABLE I

EQUILIBRIUM CONSTANTS FOR TCNE-AROMATIC COMPOUND COMPLEXES IN DICHLOROMETHANE

Compound	λ_{\max} , m μ	K	ϵ , cm. ⁻¹ m. ⁻¹ l.
4-Ethyl[2.2]PC ^a	540	52	1610
4-Acetyl[2.2]PC ^a	496	24.5	1450
4-Cyano[2.2]PC ^a	475	8	2000
<i>p</i> -Xylene ^b	460	7.6	2650

^a PC = paracyclophane; values for K determined at 25°. ^b Data from ref. 3; values for K determined at 22°.

which a ten-to-one excess of TCNE was used. Concentrations of the solutions varied from 0.01 M for the strongly complexing amino compound to 0.05 M for the relatively weakly complexing nitro derivative. The value for λ_{\max} of the TCNE-4-ethyl[2.2]paracyclophane complex was shown not to vary when the molar ratio of π -base to π -acid was varied from 40 to 0.3. Since the λ_{\max} 's all fell between 400 and 700 m μ , dramatic visual evidence for complex formation was evidenced by the color of the solutions.

The λ_{\max} of the TCNE complex of [8]paracyclophane was determined under the same conditions, and was found to be identical (λ_{\max} 492 \pm 2 m μ) with that of [9]- and [12]paracyclophane.⁹

TABLE II

CHARGE TRANSFER SPECTRAL DATA FOR TCNE-PARACYCLOPHANE COMPLEXES IN DICHLOROMETHANE AT 25°^a

Paracyclophane substituent	λ_{\max} , m μ	E_t , ^b kcal./mole	ΔE_t ^c kcal./mole
NH ₂	697 \pm 3	41.0 \pm 0.5	-13.9 \pm 0.5
OCH ₃	570 \pm 3	50.2 \pm .5	-4.7 \pm .5
OH	552 \pm 3	51.8 \pm .5	-3.1 \pm .5
C ₂ H ₅	540 \pm 2	53.0 \pm .4	-1.9 \pm .4
NHCOCH ₃	534 \pm 2	53.5 \pm .4	-1.4 \pm .4
H	521	54.9	0
Br	510 \pm 3	56.1 \pm 0.5	1.2 \pm 0.5
OAc	507 \pm 2	56.4 \pm .4	1.5 \pm .4
CONH ₂	500 \pm 1	57.2 \pm .2	2.3 \pm .2
CO ₂ H	497 \pm 2	57.5 \pm .4	2.6 \pm .4
COCH ₃	496 \pm 2	57.7 \pm .4	2.8 \pm .4
Cl	495 \pm 5	57.8 \pm .7	2.9 \pm .7
CN	475 \pm 2	60.2 \pm .4	5.3 \pm .4
NO ₂ ^d	457 \pm 5	62.7 \pm .7	7.8 \pm .7

^a One-to-one molar concentrations of TCNE and π -base unless otherwise noted. ^b Transition energy for charge transfer band. ^c E_t for TCNE-4-substituted [2.2]paracyclophane minus E_t for TCNE-[2.2]paracyclophane complex. ^d Molar concentration of TCNE to π -base was 10 to 1.

Nuclear Magnetic Resonance Spectra.—Table III records the n.m.r. data concerning the aromatic hydrogens of seven of the 4-substituted-[2.2]paracyclophanes and the parent hydrocarbon. Only one of the hydrogens was sufficiently separated in the spectrum to be identified as such, and is assigned as the hydrogen *ortho* to the functional group. This assignment is reasonable in view of the extreme dependence of its peak positions on the electronic character of the substituent. The other aromatic hydrogens exhibited considerable fine structure whose "center of gravity" could be located without difficulty through integration procedures. The τ -values of these "centers of gravity" are reported along with the range of the fine structure.

The spectrum of the TCNE complex of [2.2]paracyclophane was taken at about one molar concentration of each of the components in dichloromethane with tetramethylsilane as internal standard. The aromatic hydrogens were found to occur at 3.62 τ and the methylene hydrogens at 6.98 τ . Under the

TABLE III

NUCLEAR MAGNETIC RESONANCE SPECTRA OF AROMATIC HYDROGENS OF [2.2]PARACYCLOPHANE AND 4-SUBSTITUTED DERIVATIVES^a

Substituent	o-Hydrogen		"Center gravity" other aromatic H's		Range other aromatic H's in τ -values
	τ	No. H's	τ	No. H's	
CN ^b	3.40	6.74	3.05 to 3.60
NO ₂ ^b	2.89 ^c	1.03	3.49	6.00	3.26 to 3.52
CH ₃ CO ^d	3.22 ^c	0.99	3.60	5.86	3.37 to 3.67
Br ^d	2.97 ^e	.95	3.61	6.06	3.64 to 3.77
H ^b	3.62	7.00
C ₂ H ₅ ^d	4.00 ^f	.81	3.72	6.12	3.40 to 3.75
CH ₃ O ^d	4.56	.97	3.76	5.98	3.40 to 3.93

^a Varian Associates model A-60 n.m.r. instrument. ^b Taken in dichloromethane with hexamethyldisiloxane as internal standard. ^c Doublet. ^d Taken in carbon disulfide with hexamethyldisiloxane as internal standard. ^e Multiplet. ^f Irregular singlet.

same conditions, [2.2]paracyclophane itself gave 3.62 τ and 6.95 τ , which are within experimental error of the values obtained for the complex. Similarly, the spectra of the TCNE complex of 4-ethyl[2.2]paracyclophane and the π -base alone were compared in carbon disulfide solutions (one molar) and found to be indistinguishable within experimental error. The hydrogens of the bridging methylenes centered at 7.05 τ (multiplet), the hydrogens of the methylene side chain at 7.58 τ (multiplet), and the hydrogens of the methyl at 8.93 τ (triplet). The equilibrium constants for complex formation are such (see previous section) as to leave little doubt but that the spectrum of the complex and not uncomplexed material was being examined in those cases where TCNE was present.

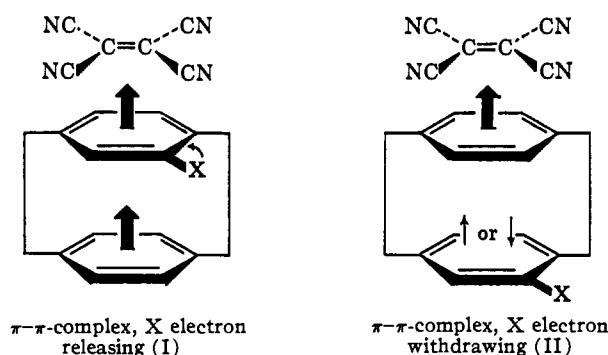
Discussion

Transannular Effects of Substituents on π -Base Strength.—The equilibrium constants for complex formation (Table I) indicate both an enhanced π -base strength for the paracyclophane system, as well as a marked sensitivity to substituent effects. Unfortunately, [2.2]paracyclophane itself was too insoluble to allow its equilibrium constant to be determined. Clearly, its K would lie between the 24.5 of the 4-acetyl and 52 of the 4-ethyl derivative, probably near 40. Thus the π -base strength of the hydrocarbon is definitely greater than that of the polynuclear hydrocarbons, naphthalene and fluorene (K = 12 and 18, respectively),³ and is probably even greater than that of pyrene (K = 30).³

In the ethyl derivative, the electron-releasing character of the ethyl group would undoubtedly make the substituted ring the more basic, and the ring which was mainly complexed (see I). The electron-withdrawing character of the acetyl and cyano groups probably deactivates the rings to which they are attached, and therefore the unsubstituted ring is undoubtedly mainly complexed, as in II. The fact that the acetyl and cyano compounds exhibit different equilibrium constants is clear evidence for transannular electronic effects of the substituents on the unsubstituted benzene ring. The equality of the equilibrium constants for *p*-xylene and 4-cyano[2.2]paracyclophane indicates that in the latter compound, the transannular electron-releasing ability of the non-complexed ring is just about cancelled by the electron-withdrawing ability of the cyano group. The equilibrium constant for 4-nitro[2.2]paracyclophane would certainly be less than that of *p*-xylene (see below), so the over-all transannular effect of the uncomplexed ring would be electron withdrawing.

In a series of structurally similar complexes, the transition energy for the charge transfer band (E_t) should

(9) D. J. Cram and R. A. Bauer, *J. Am. Chem. Soc.*, **81**, 5971 (1959).



be linear with the ionization potential of the donor (I_p). Such a relationship has been demonstrated for complexes between TCNE and a number of methylbenzenes.³ A linear relationship has also been observed between ΔF^0 of formation of the complexes and I_p of the methylbenzenes. In complexes such as II, the steric requirements for complex formation as X is changed should be constant, and in complexes such as I the steric requirements should vary only slightly. These considerations suggested that a linear relationship might exist between the transition energies for the charge transfer band (E_t) and Hammett type substituent constants, σ .

Because of the difference in nature of complexes I and II, the electron-releasing and electron-withdrawing substituents were treated separately. Figure 1 shows a plot of ΔE_t (Table II) of the electron-releasing sub-

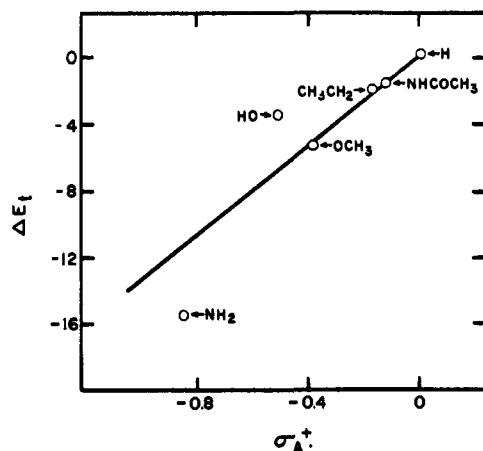


Fig. 1.—Plot of differences in transition energies between substituted and non-substituted [2.2]paracyclophane-TCNE complexes (ΔE_t values) against σ_A^+ values for electron-releasing substituents.

stituents against a series of σ_A^+ values calculated through use of Yukawa and Tsuno's¹⁰ equation (2). In this equation, σ is the revised Hammett constant,^{11a} σ^+ is the Okamoto-Brown constant^{11b} and r is a parameter which measures the importance of the resonance effect of the reaction in question. The σ_A^+ values used in Fig. 1 involved an r -value of 0.25, which provided a better fit than when r was set equal to either 0 or 0.5. Four of the substituents in Fig. 1 fall on the line, whereas the hydroxyl and amino substituents are badly off the line. These substituents are themselves known to interact directly with TCNE,¹² which fact might be responsible for their

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(11) (a) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958);

(b) Y. Okamoto and H. C. Brown, *ibid.*, **22**, 485 (1957).

(12) (a) B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman and A. F. Mower, *J. Am. Chem. Soc.*, **80**, 2806 (1958); (b) W. J. Middleton, R. E. Heckert, E. L. Little and C. G. Krespan, *ibid.*, **80**, 2783 (1958).

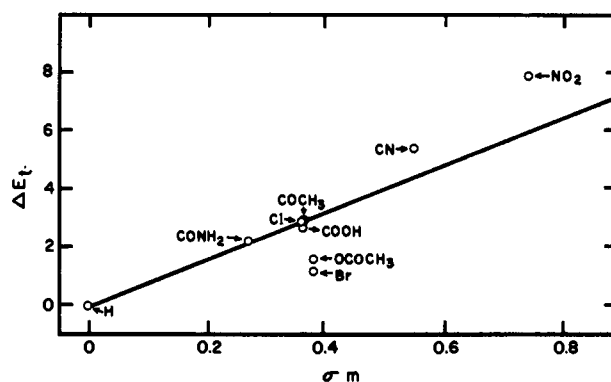


Fig. 2.—Plot of differences in transition energies between substituted and non-substituted [2.2]paracyclophane-TCNE complexes (ΔE_t values) against σ_m values for electron-withdrawing substituents.

anomalous positions on the plot. In the present study, the charge transfer band was observed to disappear slowly with time when these substituents were present. A ρ -value of -9.5 was obtained from the plot of Fig. 1.

$$\sigma_A^+ = \sigma + r(\sigma_B^+ - \sigma) \quad (2)$$

Since for electrophilic substitution on aromatic systems r -values of about unity provide the best linear free energy fits, formation of the π -salts of the present study would appear to be a poor model for electrophilic substitution.

Plots were made of the ΔE_t 's for the electron-withdrawing groups (Table II) against Hammett's revised σ_m 's and σ_p 's.^{11b} A significantly better linear fit was obtained with σ_m than with σ_p constants, and the plot involving the former is recorded in Fig. 2. This fact suggests that the transannular substituent effect has more inductive than ordinary resonance character. Since the inductive effect reflects electron displacement in σ -bonds, the transannular effect would seem to reflect the σ -character of the $2\pi\sigma$ overlap of orbitals between the aromatic nuclei of II.

Although the correlation exhibited in Fig. 2 is very crude, there is no doubt that a transannular substituent effect exists, and that the various groups fall in an order resembling that exhibited with homoannular substituent effects. The ρ obtained from the plot of Fig. 2 is -5.9 .

Effect of Deformation of Benzene Rings on π -Base Strength.—In an earlier study,⁹ the π -base strength as measured by E_t of the TCNE complexes of the [$m.n$]paracyclophanes was found to vary as the values of m and n were systematically changed from 1 to 6. Since the benzene rings of [2.2]-, [2.3]-, [3.3]- and [3.4]-paracyclophanes are bent,^{2a} the question arose as to the effect of this distortion on the π -base strength of the systems. Since the study was made, [8]paracyclophane became available⁶ whose ultraviolet absorption spectrum indicates its single benzene is bent almost as much as those of [2.2]paracyclophane.⁶ The fact that λ_{max} for the charge transfer band of the TCNE-[8]paracyclophane complex is identical with that for the unbent [12]paracyclophane complex demonstrates that distortion of about 0.1 Å. of a benzene ring from planarity^{2a} has little effect on its π -basicity. This form of distortion can no longer be invoked⁶ to explain the difference in π -base strength of the more symmetrical [$m.n$]paracyclophanes.

Interesting data have recently become available¹³ which explain the fact that the [$m.n$]paracyclophanes

(13) P. K. Gantzel, C. L. Coulter and K. N. Trueblood, *Angew. Chem.*, **73**, 755 (1960).

decrease in base strength in the order [3.3]¹⁴ > [3.4] > [2.2] > [2.3] > [6.6] > [4.4]. A three-dimensional crystallographic study of [3.3]paracyclophane¹³ has revealed that the benzene rings are not only bent, but are also considerably displaced from the centered position found in the more rigid [2.2]paracyclophane.¹⁵ The latter type of distortion reflects the strong π - π -repulsions which exist between the benzene rings, and involves distortions of most of the bond angles throughout the molecule. The π - π -repulsions are probably strongest when each benzene ring is electronically equivalent, as in the non-complexed state. When one ring becomes π -bonded to a TCNE molecule, that ring becomes slightly electron deficient, the π - π -repulsions between rings decrease, the rings become more centered, and bond angle strain is released. The same type of effect probably makes [3.4]paracyclophane a stronger π -base than [2.2]- or [3.2]paracyclophanes, whose rigidity mitigates against such distortion. The benzene rings of [4.4]paracyclophane are probably essentially planar, but are held somewhat apart by the lack of flexibility in the two 4-methylene bridges. In [6.6]paracyclophane, the longer methylene bridges allow the two benzene rings to come closer together in the complex than in that of the [4.4] compound, and hence the greater π -base strength of the larger cycle. Thus the observed order of π -base strength for the more symmetrical [*m.n*]paracyclophanes relates both to inter-ring proximity and to relaxation of internal strain in passing from π -base to π -salt.

Transannular Substituent Effects on N.m.r. Spectra of Aromatic Hydrogens.—In the n.m.r. spectra of the 4-substituted-[2.2]paracyclophanes one of the protons in the aromatic region stood apart. This proton was upfield of the others when the substituent was electron releasing, and downfield when the substituent was electron withdrawing (see Table III). This absorption is assigned to the aromatic proton adjacent to the substituent, whose chemical shift should be much more sensitive to the shielding or deshielding properties of the substituent than the other aromatic protons.^{4a,16} As in other studies^{4a} this analysis breaks down with the cyano substituent whose *ortho*-hydrogen is not separated from the others.

Of the 6 other aromatic hydrogens, 2 are in the substituted and 4 are in the transannular ring. Since the absorption bands could not be individually identified, the "center of gravity" of the absorption due to the six hydrogens is reported in Table III. This "center of gravity" moved upfield with increasing electron-releasing character of the substituent, and downfield with increasing electron-withdrawing character of the substituent. Since 4 of the 6 hydrogens are in the ring transannular to the substituted ring, this bulk shift must reflect the shift of their absorption bands as well as those of the homoannular hydrogens. A transannular effect is clearly visible in these results.

N.m.r. Spectra of TCNE Complexes of Paracyclophanes.—The n.m.r. spectra of [2.2]paracyclophane and its TCNE complex were found to be indistinguishable. The same was true for the spectra of 4-ethyl-[2.2]paracyclophane and its complex. These results indicate that only weak electron withdrawal from the aromatic systems exists in the ground state of the π -salts. This conclusion is in agreement with the valence bond picture that the wave function of the ground state

is mainly no-bond in character.¹⁷ This fact makes these π -salts poor models for transition states for electrophilic substitution at unsaturated carbon, in which much charge is created.

Experimental

4-Ethyl[2.2]paracyclophane.—To a mixture of 2.0 ml. of 6 *N* hydrochloric acid in 25 ml. of water was added 50 g. of mossy zinc, followed by 2.0 g. of mercuric chloride. The mixture was swirled to effect amalgamation and decanted. The zinc was washed 3 times with distilled water. A solution of 5.0 g. of 4-acetyl[2.2]paracyclophane⁶ in 100 ml. of acetic acid was added followed by 80 ml. of concentrated hydrochloric acid. The mixture was warmed to reflux, and after several minutes an oil separated. The mixture was refluxed for 16 hr., cooled, poured into water and extracted with pentane. The pentane extract was washed with water, sodium bicarbonate solution, water and was dried. The solvent was evaporated, and the residual solid was chromatographed on a 25 by 2.5 cm. column of alumina slurry packed in pentane. From the first 200 ml. of pentane eluate was obtained 2.7 g. of crude white solid which after two recrystallizations from hot 95% ethanol gave 1.1 g. of plates, m.p. 115–116°.

Anal. Calcd. for C₁₈H₂₀: C, 91.47; H, 8.53. Found: C, 91.58; H, 8.74.

4-Carboxamido[2.2]paracyclophane.—To 25 ml. of benzene was added 4.2 g. of 4-carboxy[2.2]paracyclophane⁶ followed by 6 g. of thionyl chloride. The mixture was heated at 95° for 1 hr., and the excess thionyl chloride and benzene were evaporated under vacuum to give 3.9 g. of waxy solid. This material was dissolved in 30 ml. of dry acetone, cooled to 5°, and 20 ml. of concd. ammonium hydroxide was added. An immediate white precipitate developed. The mixture was swirled for 5 min., 25 ml. of water was added, and the solid collected. The crude material (3.9 g., m.p. 211–213°) was recrystallized from hot chloroform to give m.p. 215–216.5°.

Anal. Calcd. for C₁₇H₁₇NO: C, 81.24; H, 6.82. Found: C, 81.14; H, 7.05.

4-Cyano[2.2]paracyclophane.—To 30 ml. of benzene was added 1.0 g. of the previously prepared amide followed by 3 g. of thionyl chloride. The mixture was refluxed for 3 hr. and the excess thionyl chloride and benzene were evaporated under vacuum to give a waxy brown solid. The product was chromatographed on a 25 by 2.5 cm. column of activated alumina slurry packed in pentane. The column was washed with 1 liter of pentane and then 500 ml. of 5% ether in pentane. The next 300 ml. of 5% ether in pentane eluted 0.4 g. of a white solid, m.p. 123.5–125°, which when recrystallized from chloroform gave m.p. 123–124°.

Anal. Calcd. for C₁₇H₁₅N: C, 87.51; H, 6.48. Found: C, 87.48; H, 6.45.

Spectra.—All ultraviolet and visible spectra were recorded at 25° on a Cary model 14 recording spectrophotometer, in either a 1.00-cm. or a 1.00-mm. cell in methylene dichloride. Scans were made from 350 to 750 m μ . All n.m.r. spectra were recorded on a Varian Associates model A-60 analytical n.m.r. spectrophotometer in either carbon disulfide or methylene dichloride (~1 *M*) with tetramethylsilane or hexamethyldisiloxane as an internal standard.

Materials.—Tetracyanoethylene was recrystallized from chlorobenzene. The other paracyclophane derivatives were available from other studies,^{5–7} and were brought to the state of purity reported.

Preparation of π -Salts.—A solution of the complex was prepared in pure methylene dichloride. Equal molar quantities of the hydrocarbon and TCNE were weighed into a 5-ml. volumetric flask, and methylene dichloride was added to the mark to give a solution of between 0.01 and 0.05 *M*. For the study of the charge-transfer spectrum of the 4-amino compound, the solvent was added just before the spectrum was recorded. This complex was the only one observed to decay with time. Within 24 hr., the color due to the charge transfer band was completely gone. Within several minutes after mixing the hydrocarbon with TCNE, the original blue color changed to green. This is presumably due to a combination of the blue charge transfer color and the yellow color of the strong absorption (end absorption) in the 350 m μ region arising from the addition compound. Ultimately only a yellow color persisted.

N.m.r. Spectra of TCNE Complexes.—Equal molar mixtures of hydrocarbon and TCNE were mixed in the appropriate solvent to give solutions about 0.5 *M*. For the [2.2]paracyclophane-TCNE complex, the spectrum was recorded in methylene dichloride because of solubility difficulties in carbon disulfide. The spectrum of 4-ethyl[2.2]paracyclophane-TCNE complex was taken in carbon disulfide.

(14) The π -base strength of [3.3]paracyclophane is estimated to be between that of 4-amino- and 4-methoxy[2.2]paracyclophane.

(15) C. J. Brown, *J. Chem. Soc.*, 3265, 3279 (1953).

(16) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p. 63.

(17) R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952).

Determination of Equilibrium Constants.—Equilibrium constants and molar extinction coefficients were determined in the manner described by Benesi and Hildebrand.^{5,6} Measurements were made at 3 points in methylene dichloride solution, at 25°, for the three compounds investigated (4-ethyl-4-acetyl- and 4-

ciano[2.2]paracyclophane). The mole fractions of the donors were varied from 0.0044 to 0.033 while the TCNE concentrations were maintained nearly constant, around 0.007 *M*. A good straight line was obtained through the three measured points for the compounds investigated.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES, LOS ANGELES 24, CALIF.]

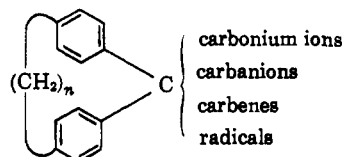
Macro Rings. XXVIII. Structure-Reactivity-N.m.r. Spectra Relationships in the [1.*n*]Paracyclophanes¹

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The [1.8]-, [1.9]- [1.10]- [1.11]- and [1.12] paracyclophanes and 4,4'-diethyldiphenylmethane were subjected to potassium *tert*-butoxide-catalyzed hydrogen-deuterium exchange in *tert*-butyl alcohol-OD at 192–208°. Exchange occurred exclusively at the diarylmethylene position. Crude rate constants for exchange were calculated. The two largest cycles exchanged with rate constants comparable to the open-chain model, but the rate constants dropped off rapidly as the cycles decreased further in size, the maximum spread being about 3 powers of 10. Similar exchange experiments demonstrated that 4-ethyl[2.2]paracyclophane underwent exchange exclusively at the non-bridging methylene position nine times faster than 2,5-dimethylethylbenzene exchanged at the comparable position. Oxidation with chromic acid of [1.8]-, [1.10]- and [1.12]paracyclophanes occurred with increasing ease in the order listed. Monoketones were isolated from the last two cycles, but the smallest cycle produced no ketone. Use of nuclear magnetic resonance (n.m.r.) spectral techniques demonstrated the carbonyl group to be attached to phenyl in the longer of the two bridges. Similar oxidation of 4,4'-diethyldiphenylmethane gave exclusively 4,4'-diethyldiphenylketone. The n.m.r. spectra of the 5 [1.*n*]paracyclophanes were taken and found to exhibit peculiarities not found in 4,4'-diethyldiphenylmethane. These reactivity and spectral characteristics of the cycles are interpreted in terms of their unusual structures.

Variation of the number of methylene groups (*n*) in the longer bridge of the [1.*n*]paracyclophanes provides a series of compounds which allow a systematic study to be made of the effect of structure on reactivity at carbon bound to two aryl groups. Of interest are changes in ease of formation of carbonium ions, carbanions, carbenes and radicals as *n* is varied.



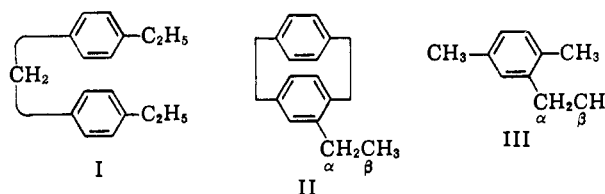
In previous work the [1.*n*]paracyclophanes with *n* = 7, 8, 9, 10, 11, and 12 were prepared in satisfactory yields with exception of the smallest cycle, whose synthesis, although achieved, was impractical.² The present study deals with the rates of carbanion formation of the [1.8]- to [1.12]paracyclophanes, as well as with the behavior of the compounds when oxidized with chromic acid. The effect of variation of *n* on the n.m.r. spectra of the hydrocarbons has also been investigated.

Results

Base-catalyzed Hydrogen-Deuterium Exchange Reactions.—The [1.8]-, [1.9]-, [1.10]-, [1.11]- and [1.12]-paracyclophanes and 4,4'-diethyldiphenylmethane (I) were subjected to hydrogen-deuterium exchange reactions in *tert*-butyl alcohol-OD with potassium *tert*-butoxide as catalyst at 192 to 208° in sealed ampoules. The amount of deuterium incorporated into the molecule and the position of exchange were determined through n.m.r. analysis. The aromatic, diarylmethylene, benzyl and remaining methylene hydrogens are well separated from one another in the spectra (see later section). Calculations of the extent of exchange for the paracyclophanes were based on the integrated absorptions, with the methylene hydrogens non-adjacent to aryl as standards. For the open-chain model, the hydrogens of the methyl group were

similarly employed. All integrations were systematically rechecked at least twice on different days. The results appear in Table I.

For purposes of comparison, 4-ethyl[2.2]paracyclophane^{3a} (II) and 2-ethyl-1,4-dimethylbenzene (III) were also subjected to exchange conditions. In the former compound, the benzene rings are known to be non-planar, and the latter compound serves as a planar model. The amounts of exchange that occurred in the bridging methylenes, in the aromatic nucleus and at



C_{α} of II could all be measured by n.m.r. techniques with the hydrogens of the β -methyl group as standard. For III, the absorptions of the β -methyl hydrogens were used as standards, and the amounts of exchange at C_{α} , at the methyl groups of the benzene ring and at the aromatic carbons were measured. Table II records the results.

The rate constants and therefore the rate factors of Tables I and II are very crude (see footnotes of tables), but the factors are large enough compared to experimental error to serve the purposes of this investigation.

Oxidation of the [1.*n*]Paracyclophanes.—To determine the relative ease of oxidation of the [1.8]-, [1.10]- and [1.12]paracyclophanes and of their open-chain model (I), the substances were treated with 1.7 equivalents of chromic acid in 97% acetic acid-3% water at 25°. The reactions were interrupted before completion and starting material and ketonic products were isolated through chromatographic procedures. The structures of the ketonic products of the reactions were determined through their n.m.r. spectra (see next section). Table III records the results. The ketone produced by oxidation of [1.11]paracyclophane was

(1) The authors wish to thank the National Science Foundation for a grant used in support of this research.

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