Anal. Calcd. for $C_{23}H_{29}ONS$: C, 75.16; H, 7.95. Found: C, 75.23; H, 7.75.

The thiomorpholide, 9.7 g., 5.2 g. of potassium hydroxide, and 40 ml. of ethanol were mixed and refluxed overnight. The reaction mixture was concentrated, diluted with water, and cautiously acidified at 0° with concentrated hydrochloric acid. The precipitate was collected, dried in a vacuum oven, and crystallized from ethanol–water to give 6.7 g. (92%) of the acid, m.p. 117–118°. For analysis, a small sample was recrystallized 3 times from ethanol–water, m.p. 119.4–120.0°.

Anal. Calcd. for $C_{19}H_{22}O_2$: C, 80.81; H, 7.85; Found: C, 80.70; H, 8.10.

1-(4-Methylphenyl)-4-(4-acetonylphenyl)-butane (XXXIII).—A solution of 3.7 ml. of methyl iodide in 15 ml. of ether was added slowly to a cooled mixture of 370 mg. of lithium ribbon in 10 ml. of ether. The mixture was then refluxed until solution of the lithium was complete (*ca.* 2 hours). The resulting solution was slowly added with vigorous stirring to a solution of 3.0 g. of 1-(4-methylphenyl)-4-(4-carboxymethylphenyl)-butane in 150 ml. of ether. The reaction mixture was stirred under reflux an additional half-an-hour, cooled in an ice-bath, and decomposed successively with water and dilute hydrochloric acid. The ether layer was washed successively with sodium bicarbonate solution and water, dried, and evaporated. The residue was chromatographed on neutral alumina to give 1.3 g. (43%) of product, m.p. 65–66°. For analysis, a small sample was recrystallized 3 times from benzene–pentane, m.p. 66.0–66.6°.

Anal. Calcd. for $C_{20}H_{24}O$: C, 85.67; H, 8.63. Found: C, 85.93; H, 8.45.

1,2,9,10,17,18-Hexabromo[2.2.2]paracyclophane (IV).—[2.2.2]Paracyclophane (II), 3.1 g., 10.8 g. of N-bromosuccinimide, 300 ml. of carbon tetrachloride and a small quantity of benzoyl peroxide were mixed and refluxed overnight. The reaction mixture was filtered, concentrated and diluted with pentane to give 7.2 g. (91%) of crude product, m.p. 250–280°. For analysis, a small sample was chromatographed and crystallized from benzene–hexane to give a discrete isomer, m.p. 303° dec. The ultraviolet spectrum of this compound exhibited a strong band at 253 mμ (ε 33,000).

Anal. Calcd. for $C_{24}H_{18}Br_6$: C, 36.68, H, 2.31. Found: C, 36.61; H, 2.43.

1,2,9,10,17,18-Dehydro[2.2.2]paracyclophane(III).–Hexabromide IV, 4.5 g., 20 g. of zinc activated with ammonium chloride and 600 ml. of ethanol were mixed and refluxed in an atmosphere of nitrogen overnight. The reaction mixture was filtered to remove zinc, diluted with water, and filtered. The solid was adsorbed on a column of neutral alumina of activity I[15] and eluted with pentane to give 820 mg. (47%) of product, m.p. 128–131°. For analysis, a small sample was repeatedly crystallized from ethanol–water, m.p. 136.0–136.8°.

Anal. Calcd. for $C_{24}H_{18}$: C, 94.08; H, 5.92. Found: C, 94.08; H, 6.06.

Catalytic Hydrogenation of 1,2,9,10,17,18-Dehydro-[2.2.2]paracyclophane (III).—Triolefin III, 100 mg., 15 mg. of platinum oxide and 50 ml. of ethanol were mixed and hydrogenated. The ethanol was filtered, concentrated, diluted with water, and cooled to give 72 mg. (71%) of [2.2.2]paracyclophane (II), m.p. 162–164°. One crystallization of this material raised the melting point to 165.0–166.6°, undepressed on admixture with an authentic sample of II.

Perhydro[2.2.2]paracyclophane (V).—[2.2.2]Paracyclophane (II), 1.0 g., 120 mg. of platinum oxide and 80 ml. of acetic acid were mixed and hydrogenated. The acetic acid was filtered and evaporated to give 750 mg. (71%) of product, m.p. 174.2–175.6°. For analysis, a small sample was recrystallized twice from ethanol, m.p. 175.2–176.0°.

Anal. Calcd. for $C_{24}H_{42}$: C, 87.19; H, 12.81. Found: C, 87.09; H, 12.72.

Treatment of Perhydro[2.2.2]paracyclophane (V) with Palladium - Carbon.—Perhydro[2.2.2]paracyclophane(V), 480 mg., was heated with 50 mg. of palladium–carbon at 310°. The reaction mixture was cooled, diluted with benzene, and filtered. Evaporation of the benzene and crystallization of the residue from ethanol gave 350 mg. (78%) of [2.2.2]paracyclophane (II), m.p. 164–166°. Admixture of this material with an authentic sample of II did not depress the melting point.

LOS ANGELES, CALIF.

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

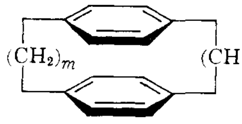
Macro Rings. XX. Transannular Effects in π–π-Complexes[1]

BY DONALD J. CRAM AND RALPH H. BAUER

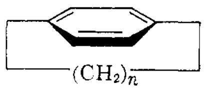
RECEIVED FEBRUARY 14, 1959

The ultraviolet absorption spectra of one-to-one tetracyanoethylene–paracyclophane charge-transfer complexes have been examined, and compared to those of open-chain models. The absorption band that occurs at the longest wave length varies with the structure of the hydrocarbon part of the 21 paracyclophane complexes studied, and ranges between extremes of 599 mμ for [3.3]paracyclophane (I, $m = n = 3$) to 476 mμ for [4.4]paracyclophane, (I, $m = n = 4$) in dichloromethane as solvent. Open-chain model compounds possess spectra that vary from 470 to 460 mμ in the position of λ_{max}. The color of the paracyclophane complexes in solution varies from yellow-orange to blue. The positions of λ_{max} (long wave length) for the complex of [3.4]paracyclophane (I, $m = 4$, $n = 3$) range between the limits of 540 mμ in chloroform to 450 mμ in *t*-butyl alcohol as the solvating power and acid-base character of the solvent is changed. A number of solid complexes were isolated and characterized. The differences in spectra between the different complexes and between the same complexes in different solvents is interpreted in terms of the ability of the non-complexed ring to delocalize positive charge in the ground and excited states of the complex. The infrared spectrum of the complex of [3.4]paracyclophane-tetracyanoethylene is different in important respects from those of either component taken separately.

In earlier papers of this series, the preparation of 18 paracyclophanes of general structure I, and 3 of general structure II has been reported.[2] The spectra[3] and reactivity[2] of compounds of structure I vary systematically as the distance between the two benzene rings is altered, and these effects have been interpreted in terms of transannular interaction of the π-electron clouds of the two aromatic nuclei with one another.



I, [m·n] paracyclophanes



II, [n] paracyclophanes

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(1) The authors wish to thank Drs. T. L. Cairns, R. E. Merrifield and W. P. Phillips for information concerning the π-acid properties of tetracyanoethylene in advance of publication.

(2) The previous paper of the series is D. J. Cram and K. Dewhirst, THIS JOURNAL, **81**, 0000 (1959).

(3) (a) D. J. Cram, N. L. Allinger and H. Steinberg, *ibid.*, **76**, 6132 (1954); (b) D. J. Cram and M. F. Antar, *ibid.*, **80**, 3103 (1958),

The discovery of tetracyanoethylene[4] (TCNE) and of its ability to enter into charge-transfer complexes with simple aromatic hydrocarbons[5] prompted the work reported here. The latter investigators[5] observed a correlation between the equilibrium constant (*K*) and the position of λ_{max} (long wave length band) of the one-to-one charge complexes between tetracyanoethylene (TCNE) and a series of ten methyl-substituted benzenes. The data allowed the relative π-base strength of the hydrocarbons to be measured.

The objectives of the present investigation were: (1) to determine if the complexes of compounds of type I, involve one or two moles of tetracyanoethylene: (2) to obtain correlations between structures of the π-bases and the energies of transitions of the charge-transfer bands; (3) to determine the effect of solvent on the energies of these transitions.

Composition of the Paracyclophane–TCNE Complexes.—Crystalline complexes of [6.6]-, [4.4]- and [3.4]paracyclophanes (I with $m = n = 6$, $m = n = 4$ and $m = 3$, $n = 4$, respectively) were prepared in two ways. In the first method, needle-like crystals of one-to-one complexes were obtained by dissolving the two components in chloroform, and then diluting the solution with pentane. The color of these complexes differed from one another as follows: [4.4]-complex, orange; [6.6]-complex, red; [3.4]-complex, purple-black. In a second method, the components were dissolved in ethyl acetate and the solutions allowed to evaporate slowly. The best crystals formed were then recrystallized and analyzed. By this method, the [6.6]-complex was one-to-one, but the other two consisted of two moles of hydrocarbon per one mole of TCNE. These complexes appeared to be stable and could be stored without difficulty.[6]

Both solid complexes of the [4.4]paracyclophane give the same ultraviolet absorption spectrum when dissolved in dichloromethane as is obtained when the two components of the complex are dissolved separately and then mixed. The same thing is true for the two complexes of [3.4]paracyclophane, and for the single complex of [6.6]paracyclophane. These spectra all contain bands in the 380 to 600 mμ region which must be associated with a complex, since neither component alone absorbs in this region. The spectra of the complexes of the three paracyclophanes (see Fig. 1) contain two maxima in this region, which were demonstrated to be due to a one-to-one complex by the following experiments.

The ultraviolet spectra of dichloromethane solutions of each of the above three paracyclophanes mixed with different proportions of TCNE were determined. In each case, solutions were prepared in which the molar concentration of added TCNE was about 15 times that of the added hydrocarbon on the one hand, and in which the molar concentration of added hydrocarbon was about 7 times that of TCNE on the other. For a particular paracyclophane complex, the positions of λ_{max}, the shapes of the curves and the relative intensities of the two absorption bands were virtually the same for the kinds of solutions. A second series of dichloromethane solutions of complexes of [2.2] and [6.6]paracyclophanes were prepared. In the first series, the concentration of TCNE was twice that of the paracyclophane, and in the second, the concentration of the paracyclophane was twice that of TCNE. The concentration of minor component in one series was equal to the concentration of the minor component in the second series. The absorbance at the two λ_{max}'s in the spectra of each paracyclophane–TCNE complex was the same in the first as in the second series. These experiments demonstrate that in solution, the observed spectrum is that of a one-to-one complex. It had been demonstrated previously by Merrifield and Phillips[5] that in solution, a one-to-one complex is formed between TCNE and various methylated benzenes.[7]

Ultraviolet Absorption Spectrum of the Paracyclophane–TCNE Complexes in Dichloromethane.—The spectra of 18 complexes whose hydrocarbon components correspond to general structure I, and 3 complexes whose hydrocarbon components correspond to II were determined. All of these complexes gave two absorption maxima except those of the [2.2]-, [2.3]- and [2.4]paracyclophanes, which exhibit only the longer wave length maximum. The shorter wave length maxima for all of the complexes lay between 416 and 430 mμ except those of the [3.3]- and [3.4]paracyclophanes, which occurred at 486 and 470 mμ, respectively. The maxima which occurred at longer wave lengths ranged from 476 mμ for the [4.4]-paracyclophane to 599 mμ for the [3.3]paracyclophane complex, while the values for the other nineteen complexes lay between these extremes. Figure 1 records typical curves obtained for these complexes, and for *p*-xylene, which serves as a primary model for these substances. Table I records the position of λ_{max} of the longer wave length band for the complexes of the paracyclophanes. For comparison, the positions of λ_{max} of the longer wave length band for the complexes of open-chain model hydrocarbons and of various methylated benzenes taken from the data of Phillips and Merrifield[5] are also included. Unfortunately, insufficient amounts of the paracyclophanes were available for determinations of the dissociation constants (*K*'s) and ϵ's of the complexes. The *K*'s of the complexes of the methylated benzenes[5] are included for reference purposes.

For TCNE complexes of structurally related hydrocarbons such as the methylated benzenes, or a series of compounds such as benzene, diphenyl, *p*-terphenyl, a relationship exists between the position of λ_{max} of the long wave length band and the dissociation constant (*K*) of the complex.[5] If the series of complexes are arranged in order of

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[4] T. L. Cairns, R. A. Carboni, D. D. Coffman, V. A. Engelhardt, R. E. Heckert, E. L. Little, E. G. McGreer, B. C. McKusick, W. J. Middleton, R. M. Scribner, C. W. Theobald and H. E. Winberg, THIS JOURNAL, **80**, 2775 (1958).

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

[6] Solid complexes made from hydrocarbons such as durene, which possess a significant vapor pressure at room temperature, slowly disintegrate and deposit minute crystals of TCNE on their surface (A. Bekoe and K. N. Trueblood, private communication).

[7] A solid complex which contains two moles of hexamethylbenzene and one mole of TCNE has been prepared (L. Smithson and K. N. Trueblood, private communication).

TABLE I

POSITION OF LONGEST WAVE LENGTH BAND IN ULTRAVIOLET ABSORPTION SPECTRUM OF DICHLOROMETHANE SOLUTIONS OF HYDROCARBON–TCNE COMPLEXES[a]

TCNE-paracyclophane complexes		TCNE-hydrocarbon complexes		
Hydrocarbon	λ_{max}, mμ	Hydrocarbon	λ_{max}, mμ	K
[3.3]	599	Hexamethylbenzene[b]	545	263
[3.4]	538	Pentamethylbenzene[b]	520	123
[1.7]	527	Durene[b]	480	54.2
[2.2]	521	1,6-Bis-(4-propylphenyl)-hexane	470	..
[3.6]	520	1,4-Bis-(4-ethylphenyl)-butane	468	..
[1.8]	515	1,3-Bis-(4-ethylphenyl)-propane	466	..
[2.3]	511	1,4-Bis-(*n*-pentyl)-benzene	463	..
[1.9]	509	Mesitylene[b]	461	17.3
[1.10]	506	1,2-Bis-(4-ethylphenyl)-ethane	460	..
		1,1-Bis-(4-*n*-propylphenyl)-methane	460	..
[1.11]	501	*p*-Xylene[b]	460	7.64
[4.6]	492	*m*-Xylene[b]	440	6.00
[9]	492	*o*-Xylene[b]	430	6.97
[12]	491	Toluene[b]	406	3.70
[6.6]	490	Benzene[b]	384	2.00
[1.12]	490	*p*-Terphenyl[b]	564	11.4
[10]	486	Diphenyl[b]	500	4.09
[5.6]	485	Benzene[b]	384	2.00
[5.5]	485	Cyclohexene	422	0.25
[4.5]	485			
[2.4]	483			
[4.4]	476			

[a] See Experimental for details. [b] Data on these complexes taken from ref. 5.

decreasing values of λ_{max}, the order is essentially the same as the order of decreasing values of K (see Table I). The paracyclophanes possess a homologous relationship to one another, and the steric requirements for complex formation should vary little from one member of the series to another. Therefore it is likely that the order of decreasing values of λ_{max} for the paracyclophane–TCNE complexes is approximately the same as the order of decreasing values for the dissociation constants for these complexes. Thus the paracyclophanes are probably arranged in Table I in roughly the order of their decreasing strength as π-bases.

The structures of these π-complexes can probably be designated[5] as one in which the face of a benzene ring occupies a plane parallel to a plane occupied by TCNE, as is pictured in III. The question of whether the carbon–carbon double bond of TCNE lies on the six-fold axis of symmetry of the benzene ring (general complex)[8] or directly over one of the carbon–carbon bonds of the benzene ring (local complex)[8] cannot be answered here. In either case, III can be used to designate the structure of the ground state, and IV the excited state of the molecule.

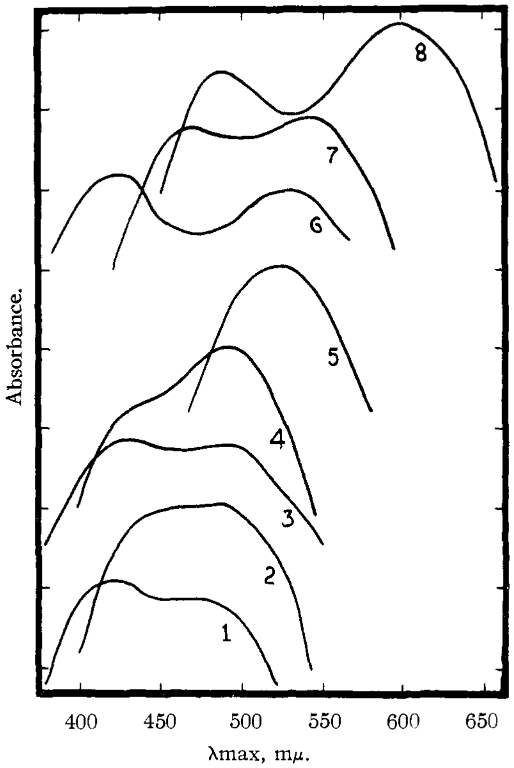
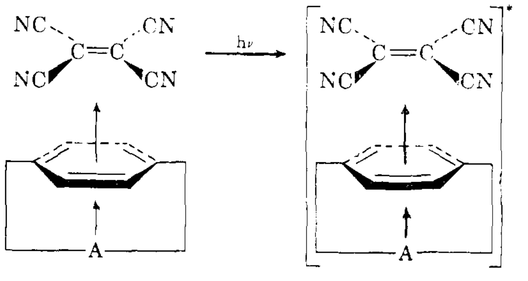


Fig. 1.—Ultraviolet absorption spectra of tetracyanoethylene–hydrocarbon complexes in dichloroethane. Curves are separated on vertical axis so they can be distinguished, and are identified by the π-base of the complex as follows: curve 1, *p*-xylene; curve 2, [4.4]paracyclophane; curve 3, [6.6]paracyclophane; curve 4, [9]paracyclophane; curve 5, [2.2]paracyclophane; curve 6, [1.7]paracyclophane; curve 7, [3.4]paracyclophane; curve 8, [3.3]paracyclophane.

Those changes in structural features of the π-base of the complexes which lower the energy of the ground state III will lower that of the excited state even more. Hence a correlation between K and λ_{max} is to be expected. In much of the following discussion, the two states will not be differentiated, since the same type of effects should apply to both.



III, ground state (less charge separation)

IV, excited state (more charge separation)

The order of arrangement of the paracyclophanes in Table I can be rationalized in terms of the effects of a number of structural features on the ability of these hydrocarbons to supply electrons to a π-acid, and to stabilize positive charge. The most important structural factors and the direction in which they are presumed to operate are listed.

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(8) E. M. Kosower and J. C. Burbach, THIS JOURNAL, **78**, 5838 (1956).

Structural factor	Effect on ability of π-base to stabilize positive charge
(1) Transannular delocalization of charge in paracyclophane	Increase
(2) Inhibition of transannular delocalization of charge due to methylene bridges holding benzene rings apart	Decrease
(3) Inhibition of transannular delocalization of charge in the π-base due to non-planar benzene rings	Decrease
(4) Inhibition of hyperconjugation of benzyl hydrogens due to bending of methylene groups out of plane of attached benzene ring, and to conformations poor for π-σ interactions	Decrease

Evidence for effect (1) is found in the fact that *all* of these complexes absorb at longer wave lengths than *any* of the open-chain model compounds. The complex of [4.4]paracyclophane absorbs at 476 mμ (the shortest wave length of any of the cyclic complexes), whereas that of 1,6-bis-(4-*n*-propylphenyl)-hexane absorbs at 470 mμ (the longest wave length of any of the model complexes). Not only can positive charge be distributed in A of III when A contains a benzene ring, but also when A contains only methylene groups, as in the complexes of [9]-, [10]- and [12]paracyclophanes. These latter complexes absorb at longer wave lengths than some of the former. When A of III contains a benzene ring, this second benzene ring can act as a π-base and complex with the first benzene ring in much the same manner as the first benzene ring complexes with TCNE. Thus these complexes resemble a multilayer sandwich in which the top layer is negative and the middle and bottom layers are positive. When A of III consists only of a methylene bridge, those methylene groups that lie over the face of the benzene ring might be able to hyperconjugate with the benzene ring and thereby absorb and stabilize charge.[9]

Effect 2 is visible in the fact that the complex of [6.6]paracyclophane absorbs at longer wave lengths than that of [4.4]paracyclophane. An examination of molecular models of the two hydrocarbons reveals that less strain is involved in pressing the two benzene rings together in the [6.6]- than in the [4.4]-hydrocarbon. In the smaller cycle, the methylene bridges are just long enough to hold the benzene rings apart, and in the larger, the bridges are long enough to permit the benzene rings to fold in toward one another. The [5.5]paracyclophane is in between the other two. As a result, transannular delocalization of charge in the complexes decreases in the order, [6.6]-complex > [5.5]-complex > [4.4]-complex.

In general, the closer the π-electron systems of the two benzene rings are to one another, the greater should be the ability of the system to stabilize positive charge. However, the more symmetrical paracyclophanes fall in the following order with respect to their ability to release electrons to TCNE: [3.3] > [3.4] > [2.2] > [3.6] > [2.3] > [4.6] > [6.6] > [5.6] $\sim$ [5.5] $\sim$ [4.5] > [2.4] > [4.4]. Thus the [2.2]-compound is a poorer π-base than the [3.3]-homolog. In [2.2]paracyclophane, not only are the two benzene rings warped (effect 3), but the $-C_6H_4-CH_2-CH_2$ bond angle is 166° instead of the normal 180°.[10] Furthermore, the 8 benzyl hydrogens are oriented in the worst possible direction for hyperconjugating with the benzene ring (effect 4).[11] Both of these effects are probably either absent, or relegated to a minor role in [3.3]-paracyclophane, and as a result, the complex of this cycle absorbs at longer wave lengths than that of [2.2]paracyclophane.[12]

The positions of the other more symmetrical complexes in the series reflect these same effects, combined in various ways. The relationships are summarized by placing the various sized bridges in decreasing order of their ability to enhance charge stabilization in complexes of the [*m.n*]paracyclophanes. These orders suggest

$$(CH_2)_3 > (CH_2)_2 > (CH_2)_6 > (CH_2)_5 > (CH_2)_4$$

approximate the distance between the two benzene rings in [3.3]paracyclophane. If the bond angles of this hydrocarbon are normal, the distance between the rings would be 2.52 Å.[13] Actually, the molecule is probably deformed, and the inter-ring distance somewhat greater.

In the complexes whose π-bases possess the general structure [1.*n*]paracyclophane, the smaller the value of *n*, the lower the energy of the III → IV transition. Although structural factors 3 and 4 also probably play some role, the data do not allow a differentiation of effects to be made.

In the series of complexes whose π-bases conform to the general structure, [*n*]paracyclophane, the energy of the III → IV transition increases with the following order of *n*: 9 > 12 > 10. An inspection of molecular models of these compounds reveals that for $n = 9$ and 12, the benzyl hydrogens occupy conformations more suitable for hyperconjugation than those in the model with $n = 10$. In all three models, at least four hydrogens attached to the middle of the methylene bridge are oriented close to the π-electrons of the benzene ring. When $n = 9$, these hydrogens are held closer to the ring than the other two, and are therefore in a better position for transannular hyperconjugation. The above order is interpreted in terms of an interplay between structural effects 1 and 3.

Comparison of the Transition Energies in Paracyclophane–TCNE Complexes and Model Complexes.—The data of Table II provide some impression of the magnitude of the stabilization energies associated with transannular effects in the paracyclophane–TCNE complexes. In the second column is listed the energies of the III → IV transition for the complexes of *p*-xylene, of the open-chain

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[9] J. S. Waugh and R. W. Fessenden, THIS JOURNAL, **79**, 847 (1957), have observed that the hydrogens of the methylene groups directly over the benzene ring in [10]- and [12]paracyclophane have significantly greater negative chemical shifts in the n.m.r. spectra than are found in methylene groups of ordinary compounds.

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

[11] (a) R. S. Mulliken, C. H. Rieke and W. G. Brown, THIS JOURNAL, **63**, 41 (1941); (b) R. T. Arnold and W. L. Truett, *ibid.*, **73**, 5508 (1951).

[12] A demonstration of the unusual character of the benzyl hydrogens in [2.2]paracyclophane is found in their low reactivity toward N-bromosuccinimide [see K. C. Dewhirst and D. J. Cram, THIS JOURNAL, **80**, 3115 (1958)].

[13] D. J. Cram, N. L. Allinger and H. Steinberg, *ibid.*, **76**, 3132 (1954).

models, and of the paracyclophanes. In the third column is listed the *differences* in energy of the transitions for the paracyclophane-TCNE complexes and that of the p-xylene–TCNE complex. These energies range from 2 to 14.4 kcal. per mole, and are probably mainly associated with transannular effects in the excited states of the complexes, and reflect both resonance and polarizability phenomena.

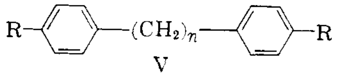
TABLE II

COMPARISON OF TRANSITION ENERGIES IN PARACYCLOPHANE-TCNE COMPLEXES AND p-XYLENE–TCNE COMPLEX[a]

π-Base	Transition energies, kcal./mole	Transition energies, $E_{p\text{-xylene–complex}}$ minus $E_{\text{paracyclophane–complex}}$
p-Xylene	62.1	..
1,4-Bis-(n-pentyl)-benzene	61.8	0.3
[10]Paracyclophane	58.8	3.3
[12]Paracyclophane	58.2	3.9
[9]Paracyclophane	58.0	4.1
1,1-Bis-(4-n-propylphenyl)-methane	62.1	0
[1.12]Paracyclophane	58.3	3.8
[1.11]Paracyclophane	57.0	5.1
[1.10]Paracyclophane	56.5	5.6
[1.9]Paracyclophane	56.2	5.9
[1.8]Paracyclophane	55.5	6.6
[1.7]Paracyclophane	54.2	7.9
1,2-Bis-(4-ethylphenyl)-ethane	62.1	0
[2.4]Paracyclophane	59.2	2.9
[2.3]Paracyclophane	55.9	6.2
[2.2]Paracyclophane	54.9	7.2
1,3-Bis-(4-ethylphenyl)-propane	61.3	0.8
[3.6]Paracyclophane	55.0	7.1
[3.4]Paracyclophane	53.1	9.0
[3.3]Paracyclophane	47.7	14.4
1,4-Bis-(4-ethylphenyl)-butane	61.1	1.0
[4.4]Paracyclophane	60.1	2.0
[4.5]Paracyclophane	58.9	3.2
[4.6]Paracyclophane	58.1	4.0
1,6-Bis-(4-n-propylphenyl)-hexane	60.9	1.2
[5.5]Paracyclophane	58.9	3.2
[5.6]Paracyclophane	58.9	3.2
[6.6]Paracyclophane	58.3	3.8

[a] Calculated from λ_{max} of the long wave length band of complex in dichloromethane as solvent.

The TCNE complexes of some of the open-chain models show stabilization energies that range from 0 to 1.2 kcal. mole. In complexes of π-bases of general structure V, these energies decrease



V

as n is changed in the following way: $n = 6 > n = 4 > n = 3 > n = 2 \sim n = 1$ The fact that any of these energies are greater than zero points to the existence of small transannular effects in complexes of these compounds. These effects grow larger as the length of the chain connecting the two aromatic nuclei increases. The longer chains allow the non-complexed benzene ring to fold back on the complexed ring without strain.

Effect of Solvent on Ultraviolet Spectrum of Paracyclophane–TCNE Complex.—A number of investigators[14] have observed solvent effects on ultraviolet spectra which are associated with charge-transfer phenomena. Kosower[8,14b,c,d] has interpreted changes in spectra with solvent in terms of the relative polarities of the ground and excited states.

In the present study, the changes in the spectra of the [3.4]paracyclophane–TCNE complex that accompanied variation in solvent were determined, and the results are recorded in Table III. A less complete investigation was also made of three other paracyclophane–TCNE complexes, and of one open-chain model. The results are summarized in Table IV.

TABLE III

EFFECT OF SOLVENT ON ULTRAVIOLET SPECTRA OF [3.4]-PARACYCLOPHANE–TCNE COMPLEX

Solvent	Maximum, mμ Longer λ	Maximum, mμ Shorter λ	Dielectric constant, (ϵ^t)[a]	t, °C.
$CHCl_3$	540	476	4.8	20
CH_2Cl_2[b]	538	473	9.1	20
CCl_4	537	459	2.2	20
C_6H_6	532	Hidden[c]	2.3	20
$(CH_2)_6$	527	453	2.0	20
$CH_3(CH_2)_3CH_3$	520	448	1.8	20
CH_3CO_2H	505[d]	454	6.2	20
$(C_2H_5)_2O$[e]	502	438[c]	4.3	20
$CH_3(CH_2)_2OH$[e]	493	409[c]	20.1	29
C_2H_5OH[e]	490	412[c]	24.3	25
$CH_3CO_2C_2H_5$[e]	483	418[c]	6.0	20
CH_3OH[e]	468	412[c]	33.6	20
CH_3CN[f]	459	416, 397	37.5	20
$(CH_3)_3COH$[e]	450	410[c]	10.9	30

[a] A. A. Maryott and E. R. Smith, Table of Dielectric Constants of Pure Liquids, *Natl. Bur. Standards*, 512 (1951). [b] TCNE in CH_2Cl_2 gives λ_{max} 297 mμ (ϵ, 13,050), 277 mμ (ϵ, 12,060) and at 300 mμ has ϵ, 679 and at 320 mμ has ϵ, <120; [3.4]paracyclophane in CH_2Cl_2 has λ_{max} 267 mμ (ϵ, 771), 259 mμ (ϵ, 609) and at 350 mμ, ϵ, 0. [c] Large band below 400 mμ. [d] Shoulder. [e] TCNE in water gives λ_{max} 411 mμ (ϵ, 461), 394 mμ (ϵ, 461), 297 mμ (ϵ, 10,600) and at 427 mμ has ϵ, 230 and at 438 mμ has ϵ, 46. [f] TCNE and acetonitrile give a light yellow color.

Tetracyanoethyene reacts with hydroxylic solvents,[15] and complexes with basic solvents such as benzene and diethyl ether.[5] However, the reactions are slow and the spectra of the solvent–TCNE complexes can be determined with reliability when their λ_{max} are equal to or greater than 440 mμ.

The data of Table III demonstrate that the position of the long wave length maximum of the [3.4]-paracyclophane–TCNE complex varies as much as 90 mμ with changes in solvent. In the first six sol-

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(14) (a) S. D. Ross and M. M. Labes, THIS JOURNAL, **77**, 4916 (1955); (b) E. M. Kosower and P. E. Klinedinst, Jr., *ibid.*, **78**, 3493 (1956); (c) E. M. Kosower, *ibid.*, **78**, 5700 (1956); (d) E. M. Kosower, *ibid.*, **80**, 3253, 3261, 3267 (1958); (e) M. Ito and N. Hata, *Bull. Chem. Soc. Japan*, **28**, 260 (1955); (f) M. Ito and W. Mizushima, *J. Chem. Phys.*, **24**, 495 (1956); (g) L. G. S. Brooker, G. H. Keyes and D. W. Heseltine, THIS JOURNAL, **73**, 5350 (1951).

(15) W. J. Middleton, R. E. Heckert, E. L. Little and C. G. Krespan, *ibid.*, **80**, 2783 (1958).

TABLE IV

EFFECT OF SOLVENT ON POSITION OF λ_{max} OF LONG WAVE LENGTH BAND IN ULTRAVIOLET SPECTRA OF PARACYCLOPHANE–TCNE AND MODEL COMPLEXES[a]

π-Base	Dichloromethane	Cyclohexane	Pentane	Acetic acid	Ethyl acetate	*t*-BuOH
[3.4]Paracyclophane	538	528	520	505	483	450
[2.2]Paracyclophane	521	497	504	495	487	468
[6.6]Paracyclophane	489	475	474	447	448	460
[4.4]Paracyclophane	475	463	452	458	447	459
1,2-Bis-(*p*-tolyl)-ethane	464	464	461	445	454	454

[a] Values are given in mμ.

vents of Table III, none of which contain basic oxygen or nitrogen atoms, the energy of the transition III → IV (long wave length band) decreases with increases in polarity of the solvent. This trend is expected, since charge is probably more separated in the excited than in the ground state.

The same trends are visible in the spectra of the other paracyclophane complexes (see Table IV). For four paracyclophane complexes, λ_{max} in dichloromethane occurs at from 12 to 24 mμ longer wave lengths than in cyclohexane or pentane. For these three solvents, [3.4] < [2.2] < [6.6] < [4.4]paracyclophane in the energy of the transitions of the complexes.

For the eight solvents of Table III which contain basic oxygen or nitrogen, no correlation appears between the polarity of the solvent and the energy of the transition. Since these solvents themselves complex with TCNE,[5] it is possible that one or two solvent molecules are specifically bound in the paracyclophane–TCNE complex, and as a result the transition under observation is not III → IV, but is VI → VII. In a sense, a complex of this sort is cross-conjugated, and the energy of the transition would be expected to depend on the acidic and basic properties of the solvent, as well as the structure of the paracyclophanes. The changes in position of λ_{max} of the four paracyclophanes in acetic acid, ethyl acetate and *t*-butyl alcohol probably reflect the interplay of these effects, as well as those discussed earlier.

$$\text{solvent}\cdots[\text{paracyclophane}\cdots\text{TCNE}]\cdots\text{solvent} \xrightarrow{h\nu}$$

VI, ground state

$$\text{solvent}\cdots[\text{paracyclophane}\cdots\text{TCNE}]^{*}\cdots\text{solvent}$$

VII, excited state

The position of λ_{max} for 1,2-bis-(*p*-tolyl)-ethane–TCNE complex is much less sensitive to solvent, and varies by only 19 mμ in the six media of Table IV.

Infrared Spectrum of the [3.4]Paracyclophane–TCNE Complex.—The infrared spectrum of the crystalline one-to-one [3.4]paracyclophane–TCNE was determined in a KBr pellet, and compared with those of [3.4]paracyclophane and TCNE separately. The bands present at 1555, 1330, 1233 and 1036 cm.$^{-1}$ in TCNE were absent in the spectrum of the complex. On the other hand, a weak band appeared at 1710 cm.$^{-1}$ in the complex spectrum that was absent in that of either component taken separately. This band occurs in the region of the C=N stretching frequency,[16] and may be indicative of bonds that possess this character in the complex.

Experimental

Starting Materials and Solvents.—The paracyclophanes and their open-chain models employed in this investigation have been reported in earlier papers of this series.[2] Tetracyanoethylene was obtained from the Central Research Department of E. I. du Pont de Nemours and Co. through the courtesy of Dr. T. L. Cairns. The solvents were Eastman Kodak Co. white label grade, or their equivalent, and they were freed of impurities when necessary by either distillation or absorption.

Preparation of Crystalline Paracyclophane–TCNE Complexes.—The one-to-one complexes of [3.4]-, [4.4]- and [6.6]-paracyclophane were prepared as follows. A solution of 0.1 g. of hydrocarbon and 0.02 g. of tetracyanoethylene in approximately 5 ml. of chloroform was prepared, and 60 ml. of pentane was added. When cooled to 0°, the resulting mixture deposited well-formed needles, which were collected and analyzed. The melting points and analyses of these complexes were as follows.

[3.4]Paracyclophane–TCNE one-to-one complex, m.p. 163–170°. *Anal.* Calcd. for $C_{25}H_{22}N_4$: C, 79.32; H, 5.76. Found: C, 80.70, H, 5.89. This complex is contaminated with a small amount of the two-to-one complex (see below).

[4.4]Paracyclophane–TCNE one-to-one complex, m.p. 170–187°. *Anal.* Calcd. for $C_{26}H_{24}N_4$: C, 79.54; H, 6.16. Found: C, 79.43; H, 6.08.

[6.6]Paracyclophane–TCNE one-to-one complex, m.p. 125–145°. *Anal.* Calcd. for $C_{30}H_{32}N_4$: C, 80.33; H, 7.19. Found: C, 80.73; H, 7.37.

An alternate method of preparing solid complexes led to the one-to-one complex with [6.6]paracyclophane, but to two-to-one complexes with the other two paracyclophanes. The general method was as follows: A mixture of 0.10 g. of hydrocarbon and 0.50 g. of TCNE was dissolved in a minimum amount of ethyl acetate, and the solution was allowed to stand for two days. During this time the solvent nearly completely evaporated to give mixtures of crystals. The best formed crystals were separated and again allowed to grow from ethyl acetate. They were dried under vacuum.

[3.4]Paracyclophane–TCNE two-to-one complex, m.p. 160–169°. *Anal.* Calcd. for $C_{44}H_{44}N_4$: C, 84.02; H, 7.05. Found: C, 83.91; H, 6.75.

[4.4]Paracyclophane–TCNE two-to-one complex, m.p. 170–185°. *Anal.* Calcd. for $C_{46}H_{48}N_4$: C, 84.10; H, 7.36. Found: C, 83.75; H, 7.15.

[6.6]Paracyclophane–TCNE one-to-one complex, m.p. 120–150°. *Anal.* Calcd. for $C_{30}H_{32}N_3$: C, 80.33; H, 7.19. Found: C, 80.29; H, 6.99.

Ultraviolet Absorption Spectral Determinations.—The spectra were recorded at 23° in a 1.000-cm. cell with a Cary, model 11 PMS recording ultraviolet spectrophotometer. The region scanned was from 350–700 mμ, and the maximum optical densities observed were approximately 1.5. Except when the relative concentrations of the two components were being varied, the solutions were made up as follows. Approximately 0.015 g. of TCNE was accurately weighed in a 5-ml. volumetric flask, and a small amount of solvent was added to see if any color appeared (a faint yellow color appeared in benzene and acetonitrile). About 0.015 g. of accurately weighed hydrocarbon was added, and the solution was diluted to the mark.

The error in determining the wave length depended on the relative flatness of the curve, and on the concentration of the complex. In 10 successive determinations of the long-wave length maximum of the [3.4]paracyclophane–TCNE complex in dichloromethane, it was demonstrated that the wave length reading varied by ±1.5 mμ. The absorption maximum of this complex was rather well defined. With the most flat maxima, the largest reading fluctuations were ±3 mμ.

The colors observed for the complexes in dichloromethane varied from deep blue for the complex of [3.3]paracyclophane to light yellow-orange for the complex of [4.4]paracyclophane.

The following experiments demonstrated that only one complex was under observation. Two solutions of [3.4]-paracyclophane and TCNE in dichloromethane were prepared, one of which contained a molar ratio of TNCE to

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[16] L. J. Bellamy, The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 226.

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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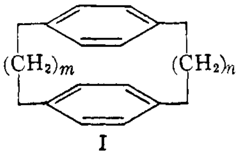
Nitration of [2.2]paracyclophane gave besides the mononitro derivative, two dinitro compounds, one mononitro phenol and two dinitrophenols. Nitration of 4-acetamido[2.2]paracyclophane gave two mononitro derivatives. Structures for these compounds are suggested which depend on their physical and chemical 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.



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[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).