Macro Rings. XL. Transannular Interactions in the Tetracyanoethylene Complexes of [3.3]Paracyclophane and Derivatives[1]

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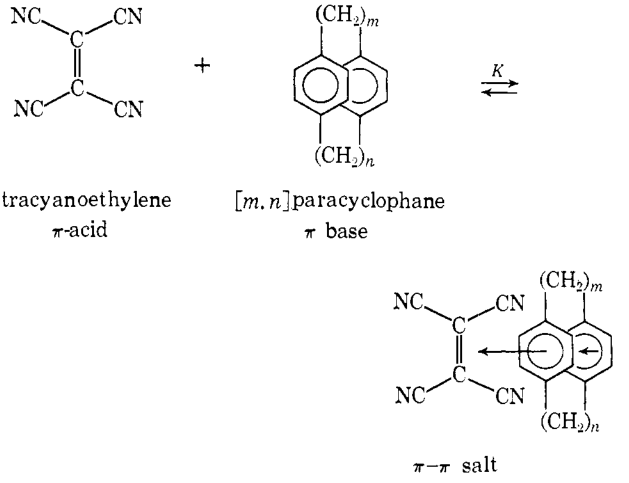
Abstract: Equilibrium constants for 1:1 π-salt formation between tetracyanoethylene and [3.3]-, [3.4]-, [2.2]-, [1.9]-, [9]-, [4.4]-, and [6.6]paracyclophane were found to decrease in value in the order listed, the values being higher than that for the open-chain model compound, 1,3-bis(4-ethylphenyl)propane. A rough linear correlation between the equilibrium constants and the position of the λ_{max} of the long-wavelength charge-transfer band in the visible spectrum of the π-salts has been observed for these and four monosubstituted [2.2]paracyclophanes. An exception to the correlation was the π-salt of [4.4]paracyclophane. The positions of λ_{max} values of the long-wavelength charge-transfer band of the π-salts of 13 substituted [3.3]paracyclophanes were determined. Possible correlations between ΔE_t's (differences in electronic transition energies between the 5-substituted [3.3]paracyclophanes and [3.3]paracyclophane itself) and substituent constants were examined. A rough linear correlation was observed between ΔE_t values and σ_m constants for the electron-withdrawing substituents. The nonsubstituted ring was the more basic of the two, and was probably the main site of salt formation. This correlation demonstrates the presence of transannular electronic effects in the [3.3]paracyclophane system. Comparison of the slope of the plot for the [3.3]-paracyclophane derivatives with the formerly determined slope of the plot for the [2.2]paracyclophane derivatives demonstrated the transannular effects in the latter system to be greater. An even poorer linear correlation was observed between ΔE_t of π-salts of [3.3]paracyclophane substituted with electron-providing groups and $\sigma_A{}^+$ ($r = 0.25$) values. From its ΔE_t value the acetamido substituent appeared to function as a moderately strong electron-withdrawing group when attached to [3.3]paracyclophane, whereas its σ_m value indicates that the group should be a weak electron donor. This abnormal behavior was also observed for 5-acetamido[3.4]paracyclophane, but not for 4-acetamido[2.2]paracyclophane. The 1:1 tetracyanoethylene–[3.3]paracyclophane salt was prepared in a crystalline form and analyzed.

The formation of stable π–π-salts between tetracyanoethylene[2] (TCNE) and the [*m.n*]paracyclophanes[3a] provided a simple means of investigating the change in the π-base strength of the aromatic hydrocarbons with changes in values of *m* and *n*,[3a] and with changes in substituents on the aromatic nucleus of [2.2]paracyclophane.[3b] The relative basicities of the cycles were estimated making use of the transition energies (E_t's) of the long-wavelength charge-transfer bands in the visible absorption spectra of the π–π-salts. Results of Merrifield and Phillips[4] established a correlation between the equilibrium constant (K) for π–π-salt formation between methylbenzenes and TCNE and the λ_{max} of the charge-transfer band of the salt. Application of this correlation to include the [*m.n*]paracyclophanes led to the π-base order [3.3]- > [3.4]- > [2.2]- > [6.6]- > [4.4]paracyclophane.[3a] Application of the correlation to 4-substituted [2.2]paracyclophanes demonstrated that electron-withdrawing substituents in one benzene ring deactivated the other ring toward salt formation.

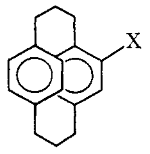


tetracyanoethylene
π-acid

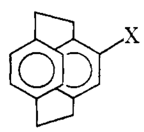
[*m.n*]paracyclophane
π base

π–π salt

The objective of the present study was twofold: to establish the π-base orders of the paracyclophane hydrocarbons by determination of the equilibrium constants with TCNE; to compare the importance of transannular effects on π basicity of the 5-substituted [3.3]paracyclophanes (IV) with those of the 4-substituted [2.2]paracyclophanes (V). The two parent hydrocarbon systems possess geometries that differ in important respects as revealed by their X-ray crystal



5-X[3.3]paracyclophane (IV)



4-X[2.2]paracyclophane (V)

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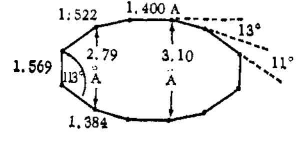
[1] The authors wish to thank the National Science Foundation for a grant used in support of this research. M. S. also wishes to thank the National Science Foundation for a National Science Foundation Predoctoral Fellowship, 1965–1969.

[2] T. L. Cairns, R. A. Carboni, D. D. Coffman, V. A. Engelhardt, R. E. Heckert, E. L. Little, E. G. McGeer, B. C. McKusick, W. J. Middleton, R. M. Scoibner, C. W. Theobald, and H. E. Winberg, *J. Am. Chem. Soc.*, **80**, 2775 (1958).

[3] (a) D. J. Cram and R. H. Bauer, *ibid.*, **81**, 5971 (1959); (b) L. A. Singer and D. J. Cram, *ibid.*, **85**, 1080 (1963).

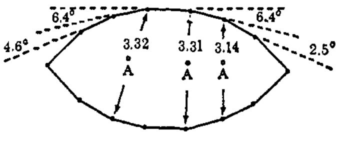
[4] R. E. Merrifield and W. D. Phillips, *ibid.*, **80**, 2778 (1958).

structures.[5] In [2.2]paracyclophane the four methylene carbons and the aromatic carbons to which they are attached all occupy the same plane, and the two benzene rings are centered. In [3.3]paracyclophane the six methylene carbons describe an elongated chair (or chaise lounge), and the two benzene rings are displaced from a centered position by 0.19 Å along the longer axis and 0.44 Å along the shorter axis of the molecule. As expected, [2.2]paracyclophane possesses considerable strain energy, which combustion indicates to be 31.3 kcal/mol.[6a] The strain energy of [3.3]paracyclophane has been calculated[5c] to be about 7 kcal/mol, and combustion indicates it to be 12 kcal/mol.[6b]



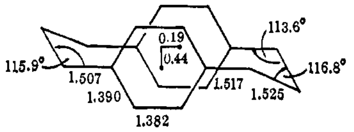
I

Crystal structure of [2,2]paracyclophane



II

Crystal structure of [3.3]paracyclophane



III

Crystal structure of [3.3]paracyclophane

Results

Starting Materials. From previous investigations samples were available of [2.2]-,[7a] [3.3]-,[7b] [3.4]-,[7c] [4.4]-,[7d] [6.6]-,[7e] [1.9]-,[7f] and [9]paracyclophane,[7g] as well as the open-chain model compound, 1,3-bis(4-ethylphenyl)propane.[7a] A sample of [8]paracyclophane was prepared as before,[8a] and the 5-substituted [3.3]paracyclophanes were available from a prior study.[8b]

Equilibrium Constants. Equilibrium constants in dichloromethane between one molecule of TCNE and one molecule of each paracyclophane on the one hand and the π–π-salts on the other were measured as previously described[3b] making use of the Benesi–Hildebrand equation[9] (1). In this equation (A) is the initial concentration of the π-acid, [D] is the initial mole fraction of π-base, l is the light path in centimeters, ϵ is the apparent molar extinction coefficient of the charge-transfer band of the π–π-salt, I_0/I is the absorbance of the mixture, and K is the equilibrium constant. Equation 1 holds only for the condition that [D] $\gg$

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

[DA], where [DA] is the mole fraction π–π-salt. Plots of (A)l/log (I_0/I) *vs.* 1/[paracyclophane] gave good straight lines whose slopes provided the equilibrium constants of Table I. The values for K and ϵ for the complexes were determined by least-squares analysis of the data. A number of other equilibrium constants taken from other studies[3b,10] are included in Table I for purposes of comparison. Four points were taken that represented mole fraction changes of the π-base that ranged from about 0.010 to 0.033, and concentration changes of TCNE that ranged from between 0.007 and 0.011 M. The purple-black π–π-salt between TCNE and [3.3]paracyclophane was prepared in a crystalline state, and was found to be 1:1 by combustion analysis.[11] In previous studies[3] a number of other crystalline π–π-salts of the [*m.n*]paracyclophanes were prepared and analyzed. Attempts to determine K for TCNE plus [8]paracyclophane were frustrated by a slow disappearance of the charge-transfer absorption band.

Table I. Correlation between Equilibrium Constants (K of TCNE + Hydrocarbon $\rightleftarrows$ π–π-Salts) and Longest Wavelength Charge-Transfer Bands in the Visible Spectrum in Dichloromethane at 25° of the π–π-Salts

Hydrocarbon	K	λ_{max}, mμ	ϵ, l. cm^{-1} mol^{-1}
[3.3]Paracyclophane[a]	79 ± 12	599	1800 ± 300
[3.4]Paracyclophane[a]	52 ± 2	538	1900 ± 100
[2.2]Paracyclophane[b]	42	521	
[1.9]Paracyclophane[a]	19 ± 2	509	1720 ± 150
[9]Paracyclophane[a]	16 ± 4	492	1000 ± 200
[6.6]Paracyclophane[a]	13 ± 1	490	2690 ± 100
[4.4]Paracyclophane[a]	36 ± 1	476	1650 ± 50
1,3-Bis(4-ethylphenyl)propane[a]	13 ± 2	477	1180 ± 150
4-Ethyl[2.2]paracyclophane[c]	52	540	1610
4-Acetyl[2.2]paracyclophane[c]	24.5	496	1450
4-Cyano[2.2]paracyclophane[c]	8	475	2000
Hexamethylbenzene[d]	263	545	4390
Pentamethylbenzene[d]	123	520	3270
Durene[d]	54.2	480	2075
Mesitylene[d]	17.3	461	3120
p-Xylene[d]	7.6	460	2650

[a] Values for K and ϵ determined by least-squares analysis. [b] K taken from ref 10. [c] Data taken from ref 3b. [d] Data taken from ref 4.

Charge-Transfer Bands of π–π-Salts. Table I records the longest wavelength λ_{max} values of the charge-transfer bands for TCNE–paracyclophane (and open-chain models) salts whose equilibrium constants have been determined. These data together with the equilibrium constants serve as a basis for possible correlation of transition energies and equilibrium constants (see Discussion).

Table II contains the λ_{max} values and transition energies of the longest wavelength charge-transfer bands of the π–π-salts between TCNE and 13 monosubstituted [3.3]paracyclophanes. Included for purposes of comparison are the previously published[3b] values for the 13 salts of monosubstituted [2.2]paracyclophanes carrying the same substituents. The λ_{max} values were all determined in dichloromethane containing equimolar mixtures of TCNE and paracyclophanes, with concentrations that ranged from 0.00519

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(5) (a) C. J. Brown, *J. Chem. Soc.*, 3265 (1953); (b) P. Gantzel, C. L. Coulter, and K. N. Trueblood, *Angew. Chem.*, **72**, 755 (1960); (c) P. Gantzel and K. N. Trueblood, *Acta Cryst.*, **18**, 958 (1965).

(6) (a) R. H. Boyd, *Tetrahedron*, **22**, 119 (1966); (b) R. H. Boyd, private communication.

(7) (a) D. J. Cram and H. Steinberg, *J. Am. Chem. Soc.*, **73**, 5691 (1951); (b) D. J. Cram and R. C. Helgeson, *ibid.*, **88**, 3515 (1966); (c) N. L. Allinger and D. J. Cram, *ibid.*, **76**, 2362 (1954); (d) D. J. Cram and N. L. Allinger, *ibid.*, **76**, 726 (1954); (e) J. Abell and D. J. Cram, *ibid.*, **76**, 4406 (1954); (f) D. J. Cram and M. F. Antar, *ibid.*, **80**, 3103 (1958); (g) D. J. Cram and M. F. Antar, *ibid.*, **80**, 3109 (1958).

(8) D. J. Cram, C. S. Montgomery, and G. R. Knox, *ibid.*, **88**, 515 (1966); (b) M. Sheehan and D. J. Cram, *ibid.*, **91**, 3544 (1969).

(9) H. A. Benesi and J. H. Hildebrand, *ibid.*, **71**, 2703 (1949).

(10) D. T. Longone, private communication.

(11) The crystal structure of this compound is being determined by K. N. Trueblood.

Table II. Substituent Effects on the Transition Energies for the Longest Wavelength Charge-Transfer Bands of the TCNE Salts in Dichloromethane at 25° in Which the π-Bases Were 5-Substituted [3.3]Paracyclophanes and 4-Substituted [2.2]Paracyclophanes

	5-Substituted [3.3]			4-Substituted [2.2][a]		
Substituent	λ_{max},[b] mμ	E_t,[c] kcal/mol	ΔE_t,[d] kcal/mol	λ_{max},[b] mμ	E_t,[c] kcal/mol	ΔE_t,[d] kcal/mol
NH_2	710 ± 5	40.3	−7.4	697 ± 3	41.0	−13.9
OCH_3	638 ± 3	44.8	−2.9	570 ± 3	50.2	−4.7
OH	620 ± 2	46.1	−1.6	552 ± 3	51.8	−3.1
C_2H_5	612 ± 2	46.7	−1.0	540 ± 2	53.0	−1.9
CH_3	603 ± 4	47.4	−0.3			
H	599 ± 2	47.7	0	521	54.9	0
$COCH_3$	575 ± 2	49.7	2.0	496 ± 2	57.7	2.8
Br	572 ± 3	50.0	2.3	510 ± 3	56.1	1.2
OAc	572 ± 2	50.0	2.3	507 ± 2	56.4	1.5
CO_2H	571 ± 2	50.1	2.4	497 ± 2	57.5	2.6
NHAc	560 ± 2	51.1	3.4	534 ± 2	53.5	−1.4
CO_2CH_3	552 ± 4	51.8	4.1			
CN	548 ± 2	52.2	4.5	475 ± 2	60.2	5.3
NO_2	543 ± 3	52.7	5.0	457 ± 5	62.7	7.8

[a] Data for these complexes taken from ref 3b. [b] Longest wavelength charge-transfer band. [c] Calculated from λ_{max} and the relationship $E_t = 28580/\lambda_{max}$ (kcal/mol) (see ref 3b). [d] $\Delta E_t = E_t$ for substituted π–π-salt minus E_t for unsubstituted π–π-salt.

to about 0.01 *M*. Variations in concentrations of TCNE and 5-methyl[3.3]paracyclophane from 10:1 to 1:10 produced no change in λ_{max} of the charge-transfer band. Thus, only 1:1 complexes were observed. This result coupled with similar results with substituted [2.2]paracyclophanes[3b] and the hydrocarbons themselves[3a] indicates 1:1 complexing throughout the whole series. The colors of the π–π-salts varied from blue-black for the 5-amino[3.3]paracyclophane to orange-red for 5-nitro[3.3]paracyclophane.

Because of the abnormality in the value of λ_{max} for the salt of 5-acetamido[3.3]paracyclophane (see Discussion), the values for the salts of 7-acetamido[3.4]paracyclophane[12] and *p*-acetamidotoluene were determined and found to be 505 ± 4 and 536 ± 2 mμ, respectively.

Discussion

π-Base Strengths of Paracyclophanes and Open-Chain Model Compounds. In Figure 1 is plotted the values of λ_{max} (in mμ) against the equilibrium constants for the π–π-salts of TCNE and the various paracyclophanes (Table I). Included is the salt of TCNE and the open-chain model compound 1,3-bis(4-ethylphenyl)propane. A general linear correlation is evident. The point farthest from the line is that for [4.4]paracyclophane, whose π-base strength is considerably higher ($K = 36$) than would be suggested by the correlation and the position of λ_{max} (476 mμ). Deviation in the opposite direction is observed for [3.3]paracyclophane whose π-base strength is somewhat lower ($K = 79$) than its λ_{max} (599 mμ) and the correlation would indicate.

The π-base strengths of the paracyclophanes (measured by the values of *K*) follow the order: [3.3] > [3.4] > [2.2] > [4.4] > [1.9] ~ [9] ~ [6.6] ~ open-chain model. This sequence is the same as that derived from the values of λ_{max}[3a] except for the relative positions of [4.4]- and [6.6]paracyclophanes. This order of change of *K* with structure provides a blend of sometimes opposing effects. If [2.2]paracyclophane is disregarded, the order for the more symmetrical paracyclophanes is [3.3]- > [3.4]- > [4.4]- > [6.6]paracyclophane ~ open-chain model. This sequence correlates with the distances of the two benzene rings from one another: the closer the two rings, the stronger the π-base strength. This correlation indicates that in the π–π-salts, the nonbound benzene ring releases electrons to the bound benzene ring, thereby enhancing the π-base character of the bound ring. This effect is more pronounced the closer the benzene rings are to one another. In [6.6]paracyclophane the benzene rings are far enough apart to act as separate entities, and the π-base strength is comparable to that of the open-chain model. This interpretation is strengthened by the fact that [9]paracyclophane, which contains no transannular ring, has a π-base strength within experimental error of the open-chain model compound.

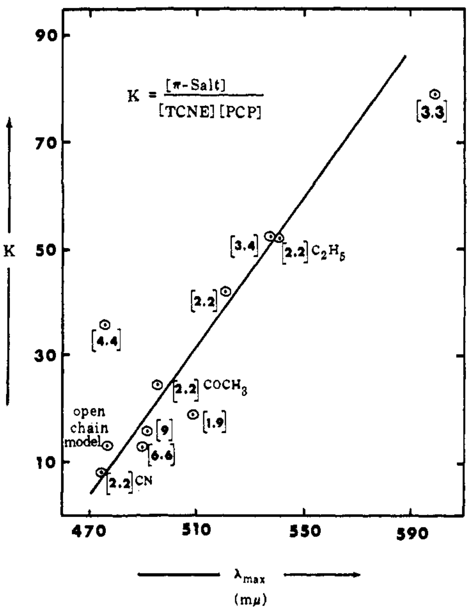

Figure 1. Plot of equilibrium constant (*K*) for salt formation against λ_{max} of long-wavelength charge-transfer band of salt.

The question now arises as to why [3.3]paracyclophane is about twice as strong a π-base as [2.2]paracyclophane, even though the two rings in the latter system are much closer together than in the former. The answer must lie in some difference in geometry of the two molecules. Several facts point to considerably

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[12] D. J. Cram, W. J. Wechter, and R. W. Kierstead, *J. Am. Chem. Soc.*, 80, 3126 (1958).

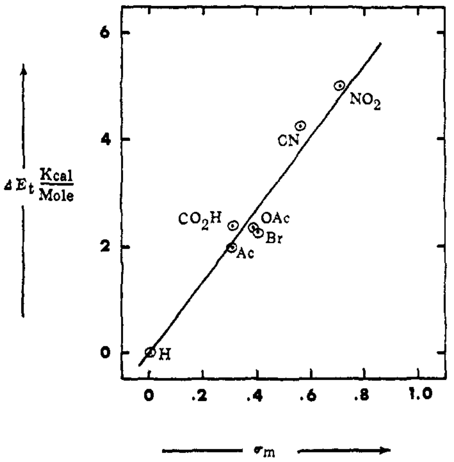


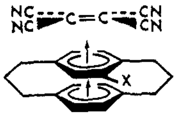
Figure 2. Plot of differences in transition energies between substituted and nonsubstituted [3.3]paracyclophane–TCNE salts (ΔE_t) against σ_m values for electron-withdrawing groups.

larger double-bond localization in the benzene rings of [2.2]paracyclophane as compared to the [3.3] homolog. In structure I,[5b] the benzene rings are centered and badly warped from their normal planar configurations. The aromatic carbon–carbon bond distances differ from one another by 0.16 Å. The aromatic hydrogen atoms are bent toward the transannular benzene ring out of the plane of their attached and the adjacent carbon atoms.[5b] The [2.2]paracyclophane molecule is 31 kcal/mol energy rich.[6a] In the structure of [3.3]paracyclophane[5c] (II and III) the rings are decentered, and are much less warped from their normal planar configurations. The aromatic carbon–carbon bond distances differ by only 0.008 Å, and the aromatic hydrogen atoms are less bent toward the transannular benzene ring out of the plane of their attached and the adjacent carbon atoms.[5c] Furthermore, [3.3]paracyclophane is closer to having a normal energy content.[5c,6b] Thus, [3.3]paracyclophane approaches normal benzene rings in intraring bond delocalization and hybridization, whereas [2.2]paracyclophane has benzene rings whose carbon atoms are between sp^2 and sp^3 hybridized. The possibility that π-basicity *decreases* with *intraring* electron delocalization but *increases* with *interring* delocalization should be considered.

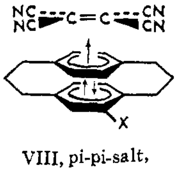
Examination of the relative π-base character of the [*m*]paracyclophanes and their open-chain model compound, *p*-xylene, provides a test for the notion that π-basicity decreases with intraring electron delocalization. In the [*m*]paracyclophanes when *m* is lower valued, the ultraviolet absorption spectrum indicates the benzene rings to be bent from their normal configurations.[8a,13] For example, the bridge-substituted carbon atoms of [9]paracyclophane probably are bent from the plane of the other four aromatic carbons by about 15°,[13] close to that of [2.2]paracyclophane. However, [9]paracyclophane is twice as strong a base as *p*-xylene, in spite of the fact that *p*-xylene has two faces and [9]paracyclophane only one. Thus, if anything, π-basicity increases with intraring electron localization, and another explanation must be sought for the fact that [3.3]paracyclophane is a stronger π-base than [2.2]paracyclophane.

Although not completely satisfactory, the best available explanation lies in the fact that [2.2]paracyclophane is a rigid molecule and [3.3]paracyclophane is a geometrically adaptable molecule. Possibly, the geometry of [3.3]paracyclophane in the π–π-salt has adjusted to provide the lowest energy electron distribution, particularly with respect to the centering of the two rings. Such adjustment is impossible for [2.2]paracyclophane π–π-salt because of the rigidity of the ring system.

Substituent Effects on π-Base Strength. The values of the transition energies for the charge-transfer bands (E_t) of Table II provide a measure of the relative π-basicities of [3.3]paracyclophane substituted with various functional groups. The steric requirements for formation of salts such as VIII should be essentially constant from compound to compound. For salts such as VII, the steric requirements should differ only slightly from compound to compound. Possibly, both complexes were formed when the substituents were neither strongly electron releasing nor withdrawing, and two charge-transfer bands might have been present. However, the intensity of the charge-transfer band of the minor component was not enough to make it visible in the spectrum, and it was probably buried beneath the major long-wavelength band which serves as the source of E_t values.



VII, pi-pi-salt,
X-electron releasing



VIII, pi-pi-salt,
X-electron withdrawing

The relationship between the π-basicity of the various substituted [3.3]paracyclophanes and the Hammett substituent constants (σ) was examined. Salts VII and VIII are intrinsically different, and therefore the compounds with electron-releasing and electron-withdrawing substituents were treated separately. Figure 2 is a plot of ΔE_t (see Table II) values of the π–π-salts against Hammett's revised σ_m values for the electron-withdrawing substituents[14] of the salts. A significantly better linear fit was observed in this than in a similar plot against σ_p values (not included). Although the correlation is far from perfect, it is good enough to establish that transannular substituent effects exist, and the various groups fall in an order similar to that observed for homoannular substituent effects.

Figure 3 is a plot of ΔE_t values of the π–π-salts substituted with electron-releasing groups against a series of $\sigma_A{}^+$ values calculated from Yukawa and Tsuno's equation (2).[15] In this equation σ^+ is the

$$\sigma_A{}^+ = \sigma_p + r(\sigma^+ - \sigma_p) \qquad (2)$$

Okamoto–Brown constant,[14b] σ_p, the Hammett constant, and r is an adjustable parameter. The value of r = 0.25 was chosen to make the slopes comparable with those of similar plots involving the substituted [2.2]paracyclophanes[3b] (see below). A reasonably good linear relationship was observed for all but the hydroxy

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(13) N. L. Allinger, L. H. Freiberg, and R. B. Herman, *J. Am. Chem. Soc.*, **85**, 1171 (1963).

(14) (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).

(15) Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc. Japan*, **32**, 965 (1959).

group, which might complex itself directly with the TCNE molecule.[16]

Comparison of Substituent Effects in the [2.2]- and [3.3]Paracyclophane Systems. Comparisons of the slopes of the plots of Figures 2 and 3 with their counterparts based on the [2.2]paracyclophane system[3b] provide measures of the relative sensitivity of the [3.3]- and [2.2]paracyclophane ring systems to homoannular and transannular substituent effects. The sensitivity of complexes of type VIII to transannular substituent effects is measured by the slope of the line of Figure 2, which is about 6.8. This value compares with one of about 8.0 obtained from a similar plot for derivatives of the [2.2]paracyclophane system. Thus, the smaller ring system shows a greater sensitivity to transannular substituent effects than the [3.3]paracyclophane whose rings are further apart. And, although [3.3]paracyclophane is itself a stronger π-base than [2.2]paracyclophane, transannular substituent effects play a more important role in the latter system. The slope of the line in Figure 3, which involves homoannular substituent effects in [3.3]paracyclophane, is about 9.1, whereas the slope of a similar plot[3b] for substituent effects in [2.2]paracyclophane is about 13.0. Thus, homoannular substituent effects are more pronounced in the more deformed [2.2]paracyclophane than in the more regular [3.3]paracyclophane ring system.

The behavior of the acetamido group is anomalous. The σ_m for this group is 0.21, and in [2.2]paracyclophane the group played its normal electron-releasing role. However, in [3.3]paracyclophane, the position of λ_{max} of the π–π-salt carrying this substituent suggests the group is between the carboxyl and carbomethoxy substituents as an electron-withdrawing group. Consequently, ΔE_t for the π–π-salt of TCNE and 7-acetamido[3.4]paracyclophane was determined ([3.4]paracyclophane was the reference compound) and found to be 3.2 kcal/mol which is almost the same as that of the corresponding salt in the [3.3]paracyclophane series. Similarly, a third ΔE_t was determined for the acetamido group from the λ_{max} of the TCNE salt of *p*-xylene and of *p*-methylacetanilide, and came to −17.1 kcal/mol. This erratic behavior of the acetamido group suggests that it itself, as well as other groups,[16] might be able to complex with TCNE directly in certain environments, such as in 5-acetamido[3.3]paracyclophane, or in 7-acetamido[3.4]paracyclophane.

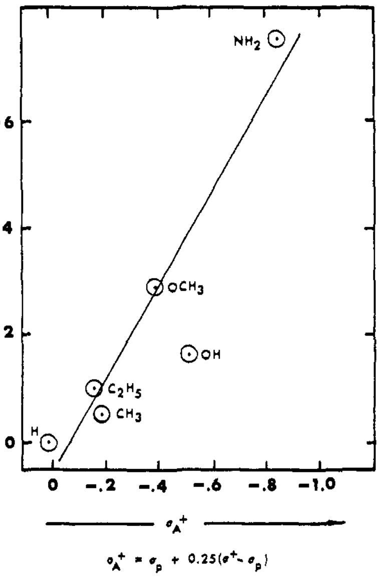
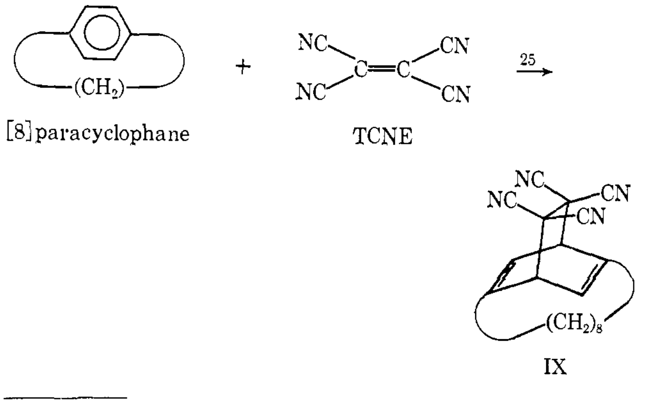


Figure 3. Plot of difference in transition energies between substituted and nonsubstituted [3.3]paracyclophane–TCNE salts (ΔE_t) against $\sigma_A{}^+$ values for electron-releasing substituents.



Anomalous Behavior of [8]Paracyclophane. An attempt was made to measure *K* for the salt of TCNE–[8]paracyclophane, but no linear plot could be obtained with eq 1. Furthermore, the original light purple methylene chloride solution of the π–π-salt turned almost colorless when allowed to stand for 3 days. These properties may be due to occurrence of a Diels–Alder reaction between the strained [8]paracyclophane molecule and TCNE to give IX. That strain in aromatic hydrocarbons lowers activation barriers for Diels–Alder type reactions is borne out by similar reactions between TCNE and [2.2]paracyclophane at relatively low temperatures.[17]

Experimental Section

Starting Materials. Reagent grade TCNE (Eastman Organics) was used without further purification. The [*m. n*]paracyclophanes were at their maximum state of purity reported in the previous investigations in which they were prepared.[7] The 5-substituted [3.3]paracyclophanes were also available from a previous study,[8b] and [8]paracyclophane was freshly prepared as previously described[8a] and purified by column chromatography.

Recording of Spectra. The ultraviolet and visible spectra used to obtain the λ_{max} values for the 5-substituted [3.3]paracyclophane TCNE salts were obtained on a Cary Model 14 recording spectrophotometer at 25° in 1.00-cm cells with reagent grade dichloromethane as solvent. Equilibrium constants were determined on a Cary Model 11 recording spectrophotometer under the same conditions. All scans covered the range from 350 to 800 mμ.

Preparation of Charge-Transfer Complexes. The complexes were prepared in dichloromethane using equimolar quantities of [3.3]paracyclophane derivative and tetracyanoethylene. The mixtures were weighed in 5-ml volumetric flasks, and dichloromethane was added to the mark to give between 0.005 and 0.01 *M* solutions. The salt of 5-amino[3.3]paracyclophane was the only one whose charge-transfer band changed with time. After 2 hr the original blue-black color had faded to dark green, and the λ_{max} of the charge-transfer band had changed from 710 to 680 mμ. After 22 hr the color had changed to light green and λ_{max} had changed to 655 mμ. Presumably, these changes are due to mixing of the blue-black color of the charge-transfer salt and the yellow color of the strong absorption band of the addition compound.

The crystalline 1:1 π–π-salt between [3.3]paracyclophane and tetracyanoethylene was prepared as follows. To a solution of 0.01 g of [3.3]paracyclophane in 15 ml of chloroform was added 0.02 g of tetracyanoethylene, followed by 60 ml of pentane. The dark blue mixture was then heated on a steam bath until it became

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homogeneous, and the volume of the solution was reduced to *ca.* 45 ml. When cooled to 0°, the mixture deposited dark brown needles, mp 186–189° (sealed tube). *Anal.* Calcd for $C_{24}H_{20}N_4$: C, 79.09; H, 5.53. Found: C, 78.86; H, 5.33.

Determination of Equilibrium Constants. The Benesi–Hildebrand treatment was used to determine the molar extinction coefficients and equilibrium constants. In a typical determination four concentrations were prepared, with the mole fraction of the donor varying from about 0.010 to about 0.033, while the concentration of the TCNE was held between 0.007 and 0.011 *M*. Good straight lines were obtained using the four points for each complex except for [3.3]- and [9]paracyclophane–TCNE salts whose *K*'s were determined only from least-squares analyses. The recorded values of the *K*'s for the other complexes were calculated both by least-squares analyses and Benesi–Hildebrand plots, and the values from each were in good agreement.

Cyclopropyl Aromatic Chemistry. I. Ultraviolet Spectra of Certain Cyclopropyl Aromatic Systems

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Abstract: The ultraviolet spectra of α- and β-cyclopropylnaphthalenes (I and II) resemble those of the corresponding methylnaphthalenes much more closely than those of α- and β-alkenylnaphthalenes. Data are tabulated to support the suggestion that a minimal electron-attracting ability of the naphthalene π system evokes a minimal conjugative response from the cyclopropyl group. To answer the question of the dependence of cyclopropane conjugation on geometry in arylcyclopropanes, uv spectra were obtained of 3- and 4-nitro-1,1a,6,6a-tetrahydrocycloprop[*a*]indenes (β- and β'-NO_2-IV), 6'- and 5'-nitrospiro[cyclopropane-1,1'-indans] (β- and β'-NO_2-V), 5-nitro-1a,2,3,7b-tetrahydro-1H-cyclopropa[*a*]naphthalene (β'-NO_2-VI), 6'-nitrospiro[cyclopropane-1,1'-tetralin] (β'-NO_2-VII), and 7- and 6-nitro-1,1a,2,3,4,8b-hexahydrobenzo[*a*]cyclopropa[*c*]cycloheptenes (β- and β'-NO_2-VIII). Values for λ_{max}'s (^1L_a band, 95% EtOH) are: β-nitroindan, 282 mμ; β-NO_2-IV and β-NO_2-V, 282; β-NO_2-VIII, 280 (nitro *meta* to cyclopropyl in β series); β'-NO_2-VIII, 285; β'-NO_2-IV, 301; β'-NO_2-VI and β'-NO_2-VII, 306; β'-NO_2-V, 313 (nitro *para* to cyclopropyl in β' series). The absence of noticeable differences in the maxima of β-nitroindan, β-NO_2-IV, and β-NO_2-V is attributed to an absence of inductive donation by the cyclopropyl group to the nitroaromatic chromophore. The bathochromic λ_{max} shifts from β-NO_2-IV to β'-NO_2-IV and from β-NO_2-V to β'-NO_2-V are seen as results of cyclopropane conjugative interaction which is possible only in the β'-nitro systems. The bathochromic λ_{max} shifts in the β' series from β'-NO_2-VIII to β'-NO_2-V are related to increasingly favorable cyclopropane geometries for conjugation. It is concluded that cyclopropane conjugation in cyclopropyl aromatic systems is a spectroscopically detectable function of cyclopropane geometry if the interacting chromophore is sufficiently electron attracting.

It is widely accepted that the functioning of a cyclopropane ring as a ground-state electron donor, as in conjugation with neighboring unsaturated systems,[2,3] in neighboring group interaction with carbonium ions,[4] and in interaction with various electrophilic reagents,[5] involves specific steric requirements for maximum effect. Increasingly, attention has been directed also to the effects of cyclopropyl substitution on the electronic spectra of π-electron systems.[6–10] Results of most of these studies indicate that cyclopropane geometry has an important effect on electronic spectral characteristics. However, for vinylcyclopropanes[9] and arylcyclopropanes,[11] geometric factors have been reported to be unimportant.

In an attempt to begin to accommodate this apparent divergence in the spectral behavior of cyclopropyl-substituted π systems, we have carried out a study of the ultraviolet spectra of a series of cyclopropyl aromatic compounds. The data presented here allow further evaluation of resonance and induction factors, and of conformation effects in cyclopropyl aromatic systems. We also discuss the role of chromophore electronegativity in affecting the auxochromic character of cyclopropanes.

Results and Discussion

Differences in ultraviolet absorption characteristics of certain α- and β-alkenylnaphthalenes have been attributed to steric interaction of α substituents with the naphthalene *peri* hydrogen, which can force the

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