A Multilayered [2.2]Paracyclophane. Synthesis and Properties

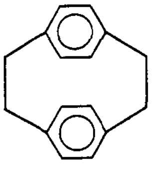
Daniel T. Longone and H. S. Chow

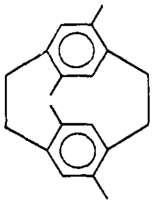
Contribution from the Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48104. *Received July 16, 1969*

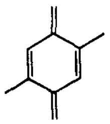
Abstract: The synthesis and properties of an extended, multilayered, benzenoid structure are described. The compound, 15,31,33,35-tetramethylheptacyclo$[28.2.2.2.^{14,17}0.^{4,25}0.^{6,27}0.^{9,20}0.^{11,22}]$hexatriaconta-1(32),4,6(27),9,11(22),-14,16,20,25,30,33,35-dodecaene (IV, stagger-ring), consists of four stacked benzenoid rings, presumably in a parallel, face-to-face arrangement and constrained by two carbon bridge bonds to lie at separations less than the normal van der Waals distance. Thus IV may be viewed as an ordered system intermediate in structural complexity between a benzenoid monomer and a multidimensional lattice. As anticipated, this unique structure exhibits ring-to-ring electronic interactions as reflected by its spectral properties and its basicity toward π acids. Compound IV was synthesized from durene in essentially six steps. The key steps involved the generation and subsequent dimerization of two homologous *p*-xylylenes, the first derived from durene and the second derived from the dimer of the first.

The [2.2]paracyclophane system I has been intensively examined since it was first obtained in 1949.[1] The unique geometry[2] of I, with nonplanar benzenoid rings at a maximum separation of only 3.1 Å, has provided a convenient substrate for the study of a variety of phenomena, particularly those of a transannular nature.[3] Since the extensive review by Smith,[3c] additional chemical probes involving each structural unit of I have been described. These include photochemical transformations,[4] additions of dienophiles to the aromatic rings,[5] generation of aryne species,[6] homolytic aromatic substitution,[7] aromatic substitutions and skeletal rearrangements *via* ionic intermediates,[8] determinations[9] of the pK_a values of hydroxy and amino derivatives, bridge chemistry,[10,11] reactions of side-chain substituents,[12] destabilization caused by eclipsing of substituents on opposed aromatic rings,[13] and an evaluation of the [2.2]-paracyclophane moiety in drug design.[14]

The closely spaced face-to-face arrangement of the aromatic rings in I has also provided a useful model for the theoretical treatment of transannular π-electron interactions and eximer emission in aromatic hydrocarbons. Recent studies include treatments of the electronic absorption and emission spectra[15] of I, the absorption spectrum of its anion,[16] and the absorption and esr spectra of the radical anion.[17] In a relevant structural probe, the strain energy has been assessed by calculation[18] and thermochemical measurement.[19]


I


II


III

It is interesting to view the benzenoid dimer I as the smallest discernible fragment of an ordered structure which maintains its integrity in solution despite serious π–π repulsions. This view led us to consider I as the simplest member of a homologous series characterized by closely spaced, fixed, parallel benzene rings—essentially lengths of a unidimensional crystal lattice. There exists the intriguing possibility that electronic effects could be transmitted over long distances in such "tight" multilayered structures. We previously described the synthesis[20] of the dissymmetric[21] 4,7,12,15-tetramethyl-[2.2]paracyclophane (II). Compound II was formed in good yield by the dimerization of the *p*-xylylene III, the latter generated by a complex series of reactions.[22] The methyl groups in II are structurally equivalent and bear the necessary *para* relationship for subsequent conversion of II to a higher homolog. We report here a detailed description[23] of the synthesis, characterization,

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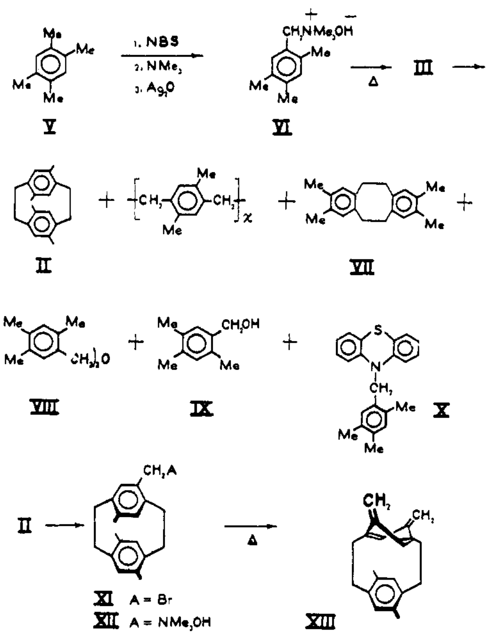
and properties of the first unequivocal example of a multilayered [2.2]paracyclophane, 15,31,33,35-tetramethylheptacyclo$[28.2.2.2^{14,17}.0^{4,25}.0^{6,27}.0^{9,20}.0^{11,22}]$-hexatriaconta-1(32),4,6(27),9,11(22),14,16,20,25,30,-33,35-dodecaene (IV, stagger-ring).

Synthesis

The Hofmann elimination route proved convenient for the preparation of large amounts of II (Scheme I).

Scheme I



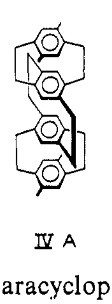
Treatment of durene (V) with a 0.5 mol equiv of N-bromosuccinimide (NBS) gave duryl bromide (59%). In repetitive brominations, the bromide was not isolated but converted to the quaternary ammonium bromide by reaction with trimethylamine. The Hofmann base VI, derived from the ammonium bromide by treatment with silver oxide, was pyrolyzed in a toluene medium and in the presence of a small amount of phenothiazine. Evolution of trimethylamine occurred smoothly and the reaction mixture afforded, as major products, the tetramethyl[2.2]paracyclophane II (*ca.* 20%) and polymer (50–60% yield). Product II is identical with the dimer obtained from the generation of *p*-xylylene III by an alternate route.[22] We have demonstrated that dimer II is the isomer shown[21] and not the alternative one with methyl groups on opposed rings in eclipsed positions. In addition to II we isolated the anticipated[13] by-products: the *o*-xylylene dimer 2,3,8,9-tetramethyl-*sym*-dibenzocyclooctadiene (VII, 0.2%); biduryl ether, VIII (1%); and duryl alcohol, IX (0.1%). These products were identified by their physical constants, combustion analysis, and spectral characterization. A major portion of the phenothiozine used in the Hofmann pyrolysis was consumed by reaction with a duryl moiety to give 10-durylphenothiazine (X). The structure of this product was confirmed by unequivocal synthesis.

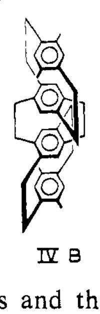
The methyl groups in II are structurally equivalent and bear the necessary *para* relationship for subsequent conversion to a *p*-xylylene moiety such as XIII. The use of Dreiding models indicates that the bridged *p*-xylylene XIII is not particularly strained relative to the [2.2]paracyclophane structure. Generation of XIII was attempted using the same Hofmann elimination route used to convert V to II. The crude monobromide XI was converted to the quaternary ammonium bromide, isolated, and characterized as the methanolate. Pyrolysis of the corresponding Hofmann base XII gave, in addition to insoluble polymer (45%), a microcrystalline hydrocarbon (mp *ca.* 265° dec) of empirical formula $C_{10}H_{11}$. Extensive characterization of the hydrocarbon confirms that it is the desired multilayered structure IV, presumably a mixture of the symmetric and dissymmetric isomers IVA and IVB. The mass spectrum of the product gives a molecular weight of 524 ($C_{40}H_{44}$) and the isotope analysis is in good agreement with $C_{40}H_{44}$. The fragmentation pattern is characteristic of [2.2]paracyclophanes[24] with major peaks for the molecular ion (73%) and the three possible *p*-xylylene ions: *m/e* 392 (57%), 262 (41%), and 132 (100%). The nmr spectrum displays the aromatic, bridge methylene, and methyl proton bands in the correct ratio of 2:6:3. More detailed spectral characterization is described below.

Properties

Molecular models of IV suggest that the inner benzenoid rings, bowed in opposite directions by *para*-paired methylene bridges, are more deformed than the outer rings. The latter rings resemble those of [2.2]-paracyclophane (I). However the total strain in IV is distributed, the compound is quite stable under ordinary conditions, both in solution and in the solid state. This is in contrast to the instability of octamethyl[2.2]-paracyclophane[13] where additional strain is introduced into the [2.2]paracyclophane system by the four pairs of eclipsed methyl groups. When heated, solid IV does decompose to give high-melting material (> 300°), presumably polymer; shock heating indicates IV has mp *ca.* 265°.

Of particular interest are those properties of IV which reflect the structural strain and the extent to which electronic interactions exist among the benzenoid rings and over an axis length of about 8–9 Å. While data are at hand which should be sensitive to these factors, the absence of detailed structural parameters permits only qualitative conclusions to be drawn. The ultraviolet absorption spectrum of IV is generally similar to those of simple [2.2]paracyclophanes and the strained octamethyl[2.2]paracyclophane[13] (see Table I). The major differences are that IV exhibits a marked hyperchromic effect in the 290-nm region and its longest wavelength band (330 nm) extends well beyond those of the models. In the spectrum of [2.2]paracyclophane, the bands at 244 and 286 nm have been associated with transannular


IV A


IV B

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[24] Substituted [2.2]paracyclophanes give as predominant fragments the corresponding *p*-xylylene (or isomeric) radical ions: D. T. Longone and G. R. Chipman, unpublished results. See also ref 3b.

Table I. Ultraviolet Absorptions of [2.2]Paracyclophanes

Compound	λ_{max}, nm (log ϵ)	
[2.2]Paracyclophane (I)	225 (4.38), 244 sh (3.52)	286 (2.41), 302 sh (2.19)
Tetramethyl[2.2]paracyclophane (II)	226 (4.20), 248 sh (3.53)	287 sh (2.38), 300 sh (2.31)
Octamethyl[2.2]paracyclophane	233 (4.21), 257 sh (3.69)	308 (2.84)
Stagger-ring IV	228 (4.30), 258 sh (3.84)	294 (3.45), 330 sh (2.65)

electronic effects and nonplanar benzene rings, respectively; the band at 302 nm has been associated with both of these factors.[25] Recent studies[15] of the absorption and emmission spectra of [2.2]paracyclophane and related structures support the idea that shifts in the ultraviolet spectra of the smaller [*m.n*]paracyclophanes are caused by configurational mixing of neutral and charge-transfer excited states. Introduction of the appropriate charge-transfer terms in the wave functions of the excited states leads to a set of energy levels with spacing in satisfactory agreement with the observed absorption spectra.

Hillier, Glass, and Rice[26] have examined in detail the absorption and emission spectra of stagger-ring IV. A shift to the red in the spectra of IV when compared to those of [2.2]paracyclophane reflects increased transannular interactions in the former compound. The calculations of Hillier, Glass, and Rice, based on the configuration interaction of neutral excited and charge-transfer states, predict the observed shifts. In addition, they have provided an interpretation of the origin of the observed transitions within the general framework developed for the [*m.n*]paracyclophanes.

Increased transannular interactions in IV, relative to model [2.2]paracyclophanes, should be evident in its role as a π base. This is indeed the case. Merrifield and Phillips[27] have examined the π complexes formed between aromatic π bases and tetracyanoethylene (TCNE). They find that in a series of structurally related bases, such as the methylated benzenes, there is a correlation between the position of the long-wavelength band and the association constant, K_x, of the complex. Increasing K_x values are paralleled by increasing λ_{max} values. This relationship has been used to assign relative π basicities to a homologous series of [*m*]- and [*m.n*]paracyclophanes.[28] Subsequent[29] determinations of K_x for certain members in these series demonstrated that the original assignments, based on λ_{max}, were generally correct. As a model for the π basicity of IV, we determined K_x for the complex of the tetramethyl[2.2]paracyclophane II and TCNE in dichloromethane. Unfortunately, IV and TCNE give a blue-black 1:1 complex which is sparingly soluble in the same medium. A rough estimate of K_x for the IV–TCNE complex was made based on the position of its long-wavelength absorption band, λ_{max} 690 nm. A linear plot[30] of K_x *vs.* the transition energy $h\nu_{max}$ using the data for the model hydrocarbons I,[31] 4-ethyl[2.2]paracyclophane,[28b] and II, gives for IV a K_x of *ca.* 630. The pertinent data are summarized in Table II. Some data from the work of Merrifield and Phillips[27] are included in the table for comparison purposes. A direct determination of K_x for the IV–1,3,5-trinitrobenzene complex was obtained in chloroform solvent. This result and related data are summarized in Table III. The value of K_x for [2.2]paracyclophane is an approximation, determined as described above and using the data of the remaining two [2.2]paracyclophanes in Table III.

Table II. Association Constants for TCNE–Aromatic Compound Complexes in Dichloromethane at 22°

Compound	λ_{max}, nm	K_x	ϵ, cm^{-1} mol^{-1} l.
Benzene[a]	384	2.00	3570
p-Xylene[a]	460	7.64	2650
Durene[a]	480	54.2	2075
Hexamethylbenzene[a]	545	263	4390
[2.2]Paracyclophane[b]	521	42	2340
4-Ethyl[2.2]paracyclophane[c]	540	52	1610
Tetramethyl[2.2]paracyclophane II	580	135	4000
Stagger-ring IV	690	(630)[d]	

[a] Reference 27. [b] Reference 31. [c] At 25°, ref 28b. [d] Calculated, see text.

Table III. Association Constants for 1,3,5-Trinitrobenzene–Aromatic Compound Complexes in Chloroform

Compound	λ_{max}, nm	K_x	ϵ, cm^{-1} mol^{-1} l.
Benzene[a]	284	0.82	9755
Toluene[a]	306	1.82	4350
Xylenes[a]	312	2.08	4080
Hexamethylbenzene[b]	390	9.6	2600
[2.2]Paracyclophane[c]	365	(2.1)[d]	
Tetramethyl[2.2]paracyclophane II[c]	405	9.6	2500
Stagger-ring IV[c]	430	21.6	1430

[a] At 25°, ref 30. [b] At 20°, R. Foster, *J. Chem. Soc.*, 1075 (1960). [c] At 22°, this work. [d] Calculated, see text.

If the order of increasing values of λ_{max} for the [*m*]- and [*m.n*]paracyclophane–TCNE complexes approximates the order of increasing values for the association constants,[28,29] then IV is the strongest π base of the hydrocarbon paracyclophanes. More significantly, it is considerably more basic than the closely related structural model II. It is unlikely that a difference in the extent of distortion of the face rings in IV and II could be responsible for their large difference in basicities. The λ_{max} for the [8]paracyclophane–TCNE complex is identical with that for the unbent [12]paracyclophane complex, suggesting that distortion of about 0.1 Å of a benzene ring from planarity has little effect on its π basicity.[28b] Clearly the enhanced basicity of IV is best explained by efficient transannular electron release to the complexed face ring by the remaining three benzenoid rings.

The nmr spectrum of IV reflects the multilayered arrangement of benzenoid rings. In $CDCl_3$ the com-

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(25) See, *e.g.*, ref 4a; also, R. Filler and E. W. Choe, *J. Am. Chem. Soc.*, **91**, 1862 (1969).

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

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

(29) M. Sheehan and D. J. Cram, *ibid.*, **91**, 3553 (1969).

(30) A. Bier, *Rec. Trav. Chim. Pays-Bas*, **75**, 866 (1956).

(31) D. T. Longone and L. G. Wolgemuth, unpublished results.

pound displays signals at τ 4.28 and 4.45 (singlets; band width at half-height, 2 Hz), 6.8–8.0 (multiplet), and 8.16 (singlet; band width at half-height, 1 Hz); the relative peak areas are 1.0, 1.0, 6.2, and 3.0, respectively (theory, 1,1,6, and 3). In CCl_4 the band positions become τ 4.38, 4.48, 6.8–8.1, and 8.19. The two singlets at *ca.* τ 4.4 are presumably due to the four aromatic protons on the outer two benzenoid rings and the four aromatic protons on the inner two benzenoid rings. These appear at considerably higher field than the aromatic protons in the tetramethyl[2.2]paracyclophane II. In CCl_4 II has bands at τ 3.78 (singlet, aromatic), 6.8–7.6 (A_2B_2 multiplet, bridge methylene), and 8.04 (singlet, methyl). The upfield shift of the aromatic protons in IV relative to those in II is anticipated considering the anisotropy effects of the two additional benzenoid rings in the structure. The magnitude of the difference (*ca.* 0.65 ppm) can be largely accounted for by this effect alone. The aromatic protons in [8]paracyclophane, with the benzenoid ring distorted about as much as those in [2.2]paracyclophane, have about the same chemical shift (τ 2.95) as do those of open-chain model structures (*ca.* τ 3.0).[28b] Consequently only small shifts of the aromatic proton resonances can be attributed to rehybridization of the benzene carbons as a result of ring deformation.[28b] In contrast, the aromatic protons in [2.2]paracyclophane appear at τ 3.56,[32] about 0.5 ppm to higher field than those of open-chain models (*e.g.*, *p*-xylene at τ 3.05). Similarly, the peak at τ 3.78 in II is shifted to higher field (0.52 ppm)[33] relative to the aromatic protons in durene (τ 3.26). In order to derive a calculated upfield shift for the aromatic protons in IV, we assume the shift of 0.5 ppm in I is due to the shielding effect of the second ring *ca.* 3.0 Å away.[2] The shielding effect of more remote rings may be approximated using the ring-current equation derived by Johnson and Bovey.[34] By this method we calculate upfield shifts of 0.15 and 0.05 ppm caused by ring currents two rings (*ca.* 6.0 Å) and three rings (*ca.* 9.0 Å) away, respectively. With II as the base structure, the calculated chemical shift for the aromatic protons on the inner two rings in IV is τ 4.4 (τ 3.78 + 0.5 + 0.15); similarly, the value for those on the outer two rings is τ 4.0. These values are in reasonably good agreement[35] with the observed singlets at τ 4.38 and 4.48.

Experimental Section

General. All melting and boiling points are uncorrected; solvents were of reagent grade quality and $MgSO_4$ was used as the drying agent for solutions. Unless otherwise indicated the nmr spectra were taken at ambient temperature on a Varian A-60 instrument using dilute solutions in carbon tetrachloride and 1% tetramethylsilane as internal standard; relative peak areas were consistent with the structures in question. The ir spectra were obtained with a Perkin-Elmer Infracord or a Perkin-Elmer spectrophotometer, Model 21; the uv and visible spectra with a Cary spectrophotometer, Model 11. Elemental analyses were by Spang Microanalytical Laboratory, Ann Arbor, Mich. and mass spectra by Morgan-Schaffer Corp., Montreal, Canada.

Duryl Bromide. A solution of 101 g (0.75 mol) of durene, 66.6 g (0.375 mol) of N-bromosuccinimide, and 0.6 g of benzoyl peroxide in 750 ml of carbon tetrachloride was refluxed for 4.5 hr and then allowed to cool. After removal of succinimide, the solution was washed with 5% sodium hydroxide solution, water, then dried and concentrated. Durene, which precipitated when the concentrate was cooled in ice, was separated and the solvent removed from the filtrate under reduced pressure. Distillation of the liquid residue afforded 47 g of duryl bromide (59%, based on N-bromosuccinimide), bp 75–78° (0.6 mm); lit.[36] 110–112° (4 mm). Its nmr spectrum has singlets at τ 2.97 and 3.10 (ArH), 5.60 (CH_2Br), 7.70 (3 H, CH_3), and 7.82 (6 H, CH_3).

Duryltrimethylammonium Bromide. The quaternary ammonium bromide was prepared by dissolving in ether the reaction residue, after solvent removal, from the above bromination and treating the resulting solution with excess anhydrous trimethylamine. In a typical run, 231 g (1.72 mol) of durene and 154 g (0.87 mol) of N-bromosuccinimide afforded 124 g (53%, based on N-bromosuccinimide) of duryltrimethylammonium bromide, mp 253–254.5° (from acetonitrile); nmr (D_2O, internal sodium 2,2-dimethyl-2-silapentane sulfonate): singlets at τ 2.63 and 2.70 (ArH), 5.45 (CH_2), 6.83 ($N{-}CH_3$), 7.58 (3 H, $ArCH_3$), and 7.70 (6 H, $ArCH_3$).

Anal. Calcd for $C_{13}H_{22}NBr$: C, 57.35; H, 8.15; N, 5.15. Found: C, 57.24; H, 8.07; N, 5.25.

Pyrolysis of Duryltrimethylammonium Hydroxide (VI). Duryltrimethylammonium bromide was treated with freshly prepared silver oxide in the usual manner[37] to afford aqueous solutions of the hydroxide VI. The general pyrolysis[38] procedure is outlined below.

An aqueous solution of the hydroxide was mixed with an equal volume of toluene in a flask fitted with a Dean-Stark trap. A small amount of phenothiazine[38] was added, the mixture heated with stirring, and water removed as the toluene–water azeotrope (84°). The system was kept at approximately constant volume by the addition of incremental volumes of toluene. Evolution of trimethylamine began when nearly all the water had been removed and it continued for 12–24 hr at the reflux temperature. After the evolution of trimethylamine had ceased or slowed significantly the mixture was allowed to cool and the polymer, which precipitates during the course of the reaction, was removed by filtration (50–60% yield, mp >300°). The filtrate was concentrated to near dryness under reduced pressure, the residue triturated with ether, the ether insoluble material (polymer) removed, and, finally, the solvent removed from the ether solution. The residue thus obtained was taken up in a small volume of pentane and chromatographed on alumina (Merck). This gave, in order of elution, a hydrocarbon fraction containing the *p*-xylylene dimer 4,7,12,15-tetramethyl-[2.2]paracyclophane (II) and, in some cases, the *o*-xylylene dimer VII, followed by fractions containing 10-durylphenothiazine (X), biduryl ether (VIII), an unidentified carbonyl-containing (ir) oil, and duryl alcohol (IX).

The solid from the hydrocarbon fraction (pentane), containing mainly II, was generally triturated with pentane or hexane to remove small amounts of the sparingly soluble dimer VII.

4,7,12,15-Tetramethyl[2.2]paracyclophane (II). After recrystallization from pentane or sublimation at 80° (0.1–0.2 mm) this dimer had mp 105–107° (lit.[20] 104–105°); yield *ca.* 20%. For another synthesis of II see ref 6b.

2,3,8,9-Tetramethyl-*sym*-dibenzocyclooctadiene (VII). After two recrystallizations from chloroform this dimer had mp 209–211° (sealed tube). When isolated, it was obtained in *ca.* 0.2% yield. The structural assignment is based on its uv (cyclohexane) and nmr ($CDCl_3$) spectra: λ_{max} 250 sh (log ϵ 2.48), 265 sh (3.06), 269 (3.22), 273 (3.16), and 279 nm (3.29); (*cf.* spectrum[13] of 1,2,3,4,7,8,9,10-octamethyl-*sym*-dibenzocyclooctadiene); singlets at τ 3.20 (ArH), 7.08 (CH_2), and 7.87 (CH_3). The ir spectrum (KBr) exhibits characteristic bands (cm^{-1}) at: 3030 (m), 2950 (s), 2865 (m), 1508 (s), 1462 (s), 1332 (m), 1030 (m), 994 (m), 929 (m), and 880 (s).

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(32) Unless otherwise stated the nmr data cited were obtained in CCl_4 solvent.

(33) That the observed shifts for I and II are identical in magnitude may reflect in II a fortuitous cancelling of substituent effects, *i.e.*, an upfield shift due to an *ortho* methyl and an equal downfield shift due to a pseudo-*gem*-methyl (see ref 3b).

(34) C. E. Johnson, Jr., and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

(35) Whatever degree of correspondence exists between the calculated and observed values may be fortuitous. The calculation model necessarily utilized assumed geometry and ring-to-ring distances in IV, based on the known structure for I. Also, it neglects secondary structural effects which may be of significant magnitude (*e.g.*, see ref 3b).

(36) W. H. Hunter and D. E. Edgar, *J. Am. Chem. Soc.*, **54**, 2025 (1932).

(37) A. C. Cope and E. R. Trumbull in "Organic Reactions," Vol. XI, A. C. Cope, Ed., John Wiley & Sons, Inc., New York, N. Y., 1960, Chapter 5.

(38) *Cf.*, H. E. Winberg and F. S. Fawcett in "Organic Syntheses," Vol. 42, V. Boekelheide, Ed., John Wiley & Sons, Inc., New York, N. Y., 1962, p 83.

Anal. Calcd for $C_{20}H_{24}$: C, 90.85; H, 9.15; mol wt, 264. Found: C, 90.79; H, 9.03; osmometric mol wt (benzene), 257.

10-Durylphenothiazine (X). This compound was eluted from the column using 10% benzene–pentane. It is a minor component of the product mixture, *ca.* 40% yield based on phenothiazine, mp 128.5–130.5° (methanol). The ir spectrum (KBr) has bands (cm^{-1}) at 1470 (vs); 1512, 1495, 1375, 1255, 1220, 740 (all s); 3105, 3045, 2945, 2875, 1600, 1580, 1330, 1290, 1130, 1040, and 870 (all m); nmr at τ 2.9–3.6 (multiplet, ArH), and singlets at τ 5.15 (CH_2), 7.70, 7.82, and 7.90 (all CH_3); uv (cyclohexane) at 257 (log ϵ 4.70) and 317 nm (3.77). This material is identical in all respects with 10-durylphenothiazine prepared[39] as described below.

Phenothiazine (20 g, 0.10 mol) was added in small portions over 10 min to sodium (2.6 g, 0.11 g-atom) in 500 ml of liquid ammonia. The mixture was stirred for 3.5 hr and then duryl bromide (32 g, 0.15 mol) was added over a period of 1 hr. After an additional 2 hr the ammonia was allowed to evaporate and the resulting residue treated with 150 ml of hot benzene. The filtered benzene solution was concentrated under reduced pressure and a portion of the resulting liquid residue subjected to column chromatography on alumina (Merck) using pentane, 10% benzene–pentane, and 50% benzene–pentane. The last solvent system gave fractions containing 10-durylphenothiazine (X). The product thus obtained (54% yield) gave mp 128.5–131° (methanol–ether).

Anal. Calcd for $C_{22}H_{21}NS$: C, 79.72; H, 6.39. Found: C, 79.70; H, 6.05.

Biduryl Ether (VIII). This material (*ca.* 1.4%) was eluted with 50% benzene–pentane (see above), mp 100–101° (pentane); lit.[40] mp 99.5–100.5°. The ir spectrum (Nujol) has characteristic bands (cm^{-1}) at 1130 (s), 900 (m), and 880 (m); nmr singlets at τ 3.01 and 3.15 (ArH), 5.62 (CH_2), and 7.80 (CH_3).

Anal. Calcd for $C_{20}H_{26}O$: C, 85.06; H, 9.28. Found: C, 85.31; H, 9.08.

Duryl Alcohol (IX). This product (0.15% yield) was eluted with methanol, mp 81.5–82° (lit.[41] 83–83.5°). In Nujol the OH band appears at 3390 cm^{-1}.

4-Bromomethyl-7,12,15-trimethyl[2.2]paracyclophane (XI) and 4-(Dimethylaminomethyl)-7,12,15-trimethyl[2.2]paracyclophane Methanobromide. A solution of 16.07 g (0.0608 mol) of II, 5.42 g (0.0304 mol) of N-bromosuccinimide, and 0.024 g of benzoyl peroxide in 550 ml of carbon tetrachloride was heated at reflux for 6 hr. After removal of succinimide, the carbon tetrachloride solution was washed and dried as described above for duryl bromide and then concentrated under diminished pressure to give a red oil. This contained as solutes (nmr) mainly unreacted II and the benzyl bromide XI. A small portion of this oil was withdrawn, all volatiles removed *in vacuo*, the oily residue taken up in pentane, and then the resulting solution chilled in ice. This treatment gave a small amount of solid whose nmr spectrum was as anticipated for the bromide XI: τ 3.43, 3.62, 3.70, and 3.89 (all singlets, ArH); an AB quartet centered at τ 5.77, J = 11 Hz and Δ_{AB} = 10.2 Hz (CH_2Br); and bands at τ 6.6–7.7 (multiplet, bridge methylenes) and 8.00 (singlet, CH_3).

The remainder of the bromination reaction concentrate was taken up in ether and treated with excess anhydrous trimethylamine. This afforded, as a precipitate, the quaternary ammonium bromide derived from XI (7.95 g, 65% based on N-bromosuccinimide). An analytical sample was prepared by chromatographing a portion of the salt on silica gel (Grace, grade 923, 100–200 mesh; 5% methanol–acetone). Material thus obtained was recrystallized from methanol–ether to give product salt as the monomethanolate, mp 239–241.5° dec.

Anal. Calcd for $C_{24}H_{36}NOBr$: C, 66.35; H, 8.35; O, 3.68. Found: C, 66.22; H, 8.31; O, 3.88.

The ir spectrum (KBr) has bands (cm^{-1}) at 3280, 1495, 1455, 1035, 880, and 710 (all s); 1625, 1605, 1380, 1250, 1200, 1170, and 970 (all m). The nmr spectrum ($CDCl_3$) exhibits peaks at τ 3.03, 3.50, 3.68, 3.92 (singlets, all ArH), an AB quartet centered at τ 5.32, J = 13 Hz, and Δ_{AB} = 8.8 Hz ($ArCH_2N$); τ 6.58 (singlet, CH_3OH), 6.72 (singlet, $N(CH_3)_3$), 6.2–7.5 (multiplet, bridge methylenes), 7.86 (singlet, 3 H, $ArCH_3$), and 7.98 (singlet, 6 H, $ArCH_3$).

Stagger-Ring IV. The quaternary ammonium bromide above, 12.7 g (0.032 mol), was dissolved in 175 ml of warm water and converted to the hydroxide by treatment with freshly prepared silver oxide. The resulting aqueous solution, after removal of solids, was added to an equal volume of toluene containing 59 mg of phenothiazine. The system was then treated as described above for the pyrolysis of VI. Evolution of trimethylamine began after nearly all the water had been removed from the system and continued for 36 hr at the reflux temperature. The reaction mixture was then allowed to cool, the precipitated polymer (45%, mp 443–445° dec) was removed, the resulting filtrate dried and then concentrated to a small volume under reduced pressure. On chilling the concentrate, crude stagger-ring IV precipitated, 0.74 g (in several crops). The solids were dissolved in a minimum amount of benzene and chromatographed on silica gel (50% benzene–hexane) to give a single-component solid (tlc, several systems). Recrystallization from the system chloroform–ether–pentane gave microcrystals (0.67 g, 8.1%), mp 264–265° dec (shock heating); ir (KBr, cm^{-1}) 3020 (m), 2950 (s), 2870 (m), 1592 (m), 1493 (m), 1460 (m), 1438 (m), 890 (s), 690 (s), and 663 (m). Additional spectral data and characterization are described in the text.

Anal. Calcd for $C_{40}H_{44}$: C, 91.55; H, 8.45. Found: C, 91.63; H, 8.36.

Other than IV and polymer, the pyrolysis products were not further examined.

Charge-Transfer Complexes. The molar extinction coefficients and association constants, K_x, as listed in Tables II and III were determined using excess π acid and as described previously.[42] At least five concentrations were utilized in each case, with molar concentrations of π base varying from about 0.001 to about 0.010 and molar concentrations of π acid varying from about 0.01 to about 0.18. The Benesi–Hildebrand plots gave good straight lines in each case and K_x values were determined from these.[43]

Strong absorption below 450 nm by the π-acid 1,3,5-trinitrobenzene and the position of the λ_{max} for its complex with I prevented a determination of K_x by this method.

The 1:1 complex of IV and TCNE was prepared by mixing a solution of 6 mg of IV in dichloromethane with one containing 3 mg of TCNE in the same solvent. The resulting deep blue solution soon deposited a blue-black precipitate. This was removed, washed with dichloromethane, and then dried to give product (3 mg), mp >340° dec.

Anal. Calcd for $C_{46}H_{44}N_4$: N, 8.58. Found: N, 8.17.

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(42) D. G. Farnum, E. R. Atkinson, and W. C. Lothrop, *J. Org. Chem.*, **26**, 3204 (1961).

(43) The K_x values reported here should be considered as approximate. Linear Benesi–Hildebrand plots do not necessarily exclude the presence of multiple equilibria, *cf.*, G. D. Johnson and R. E. Bowen, *J. Am. Chem. Soc.*, **87**, 1655 (1965).