Electro-organic Chemistry. Part 3.[1] Transannular Interaction and Reactions of 5,13-Disubstituted [2.2]Metacyclophanes: Substituent Effects on Carbon-13 N.m.r. spectra, Cyclic Voltammetric Peak Potentials, and Anodic Oxidation

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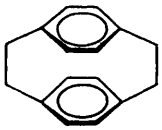
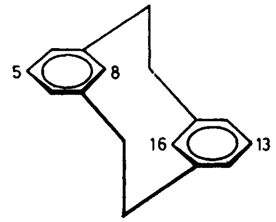
A series of 5,13-disubstituted [2.2]metacyclophanes have been prepared. Their proton and carbon-13 n.m.r. spectra have been measured. Cyclic voltammetry was conducted in acetonitrile. From these data the interaction of the substituent towards the opposing ring was estimated. The carbon-13 resonances of inner aryl carbon was found to be affected by the substituent in the other ring. Similarly the first anodic peak, E_p (O_1), and half-wave potential, $E_{1/2}$ (1), were found to be dependent on the substituent in the other ring. Remarkable voltammogram changes were noted for methoxy-derivatives. Controlled-potential electrolysis at the potential of O_1 gave good yields of the corresponding 4,5,9,10-tetrahydropyrenes.

ALTHOUGH the dependence of equilibrium constant on methylene chain length has been studied for the charge-transfer complexes formed between tetracyanoethylene (TCNE) and [2.2]paracyclophane (1) and its homologues,[2] the transannular π–π interaction in [2.2]metacyclophane (2) has been the subject of lively discussion for the last two decades.[3,4] The equilibrium constant for the complex (2)–TCNE is appreciably smaller than that for (1)–TCNE.[3] Langer and Lehner[5] have concluded that there is no transannular interaction in (2) using a tricarbonylchromium complex.



(1)

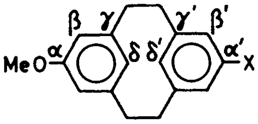


(2)

Recently, Boschi and Schmidt[6] have shown, by photoelectron spectroscopy, that there is π–π interaction in (2) although it is confined to the inner aryl positions, C-8 and C-16; this contrasts with (1) in which the interaction is extended over the aryl carbon atoms of both benzene rings.

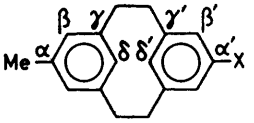
Local perturbation of the π system in (2) is also evident from the carbon-13 n.m.r. data. Previously we observed a downfield shift amounting to 6—7 p.p.m. for C-8 and C-16 carbon resonances in (2) by comparing the spectra with those of model compounds.[7,8] The shift is explained by *p*-orbital compression. In contrast, a downfield shift was observed for all protonated carbon resonances for (1) although they were smaller in magnitude. Strain energies for (1) and (2) are 31 and 12 kcal mol^{-1}, respectively, and (2) is much less strained than (1).[9] In spite of these, compound (2) and its derivatives have been shown to be highly reactive and give transannular products under extremely mild conditions.[3,10-12] Especially effective are one-electron transfer reagents[10,11] and electrochemical oxidation.[1,13]

Evidently u.v. results are not suitable to interpret the ground-state chemistry of (2). Since we wished to correlate the enhanced reactivity to other structural parameters, we examined the electronic effect of a substituent X on the electron density of the opposing *sp*^{2} carbon in a series of derivatives [(3) and (4)] by way of carbon-13 n.m.r. spectroscopy. We also subjected these compounds to cyclic voltammetry (c.v.) in order to clarify the effect of X on the ease of one-electron abstraction from another benzene ring. The correlation between the c.v. peak potential, E_p, and the carbon-13 n.m.r. chemical shift was also explored. Controlled-potential anodic oxidation to give the transannular product (5) was also examined.



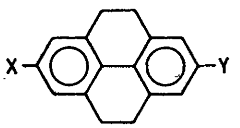
(3)

	X
a ;	MeO
b ;	Me



(4)

	X
a ;	Me
b ;	Br
c ;	CN
d ;	NO$_2$

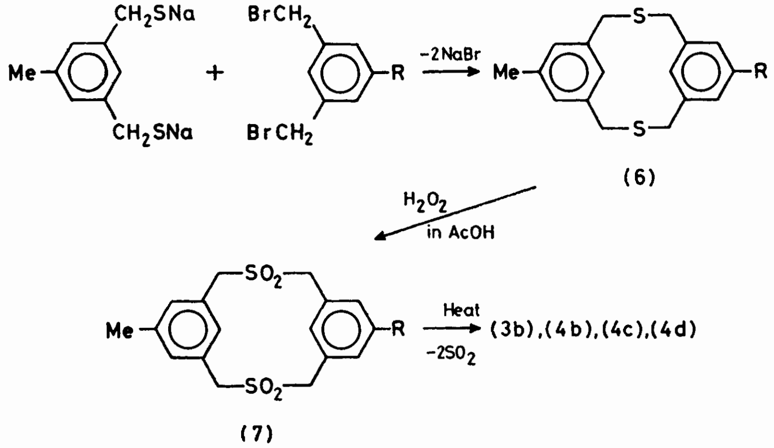


(5)

	X	Y
a ;	H	H
b ;	MeO	MeO
c ;	MeO	Me
d ;	Me	Me
e ;	Me	Br
f ;	Me	CN
g ;	Me	NO$_2$

Preparation.—Compounds (3b), (4b), (4c), and (4d) were prepared according to the general method outlined in Scheme 1. Dimethoxy (3a)[14] and dimethyl compounds (4a)[15] were prepared by the modified Wurtz coupling reaction according to the literature.

The 12-membered ring bis-sulphide (6) was obtained by the condensation, at high dilution, of α,α'-dibromo-*m*-xylene and α,α'-mesitylenedithiol in the presence of ethanolic sodium hydroxide in benzene–ethanol. The bis-sulphone (7) prepared by the oxidation of (6) was pyrolysed at 500 °C using an apparatus similar to that described by Vögtle *et al.*[16] Melting points and analytical data for new compounds are summarized in Table 1.



SCHEME 1

Proton and Carbon-13 *N.m.r.*—Except for the symmerical compounds (3a) and (4a), the newly obtained [2.2]metacyclophanes showed two sets of an AB pattern due to bridging methylene protons indicative of a rigid stepped conformation.[15] An upfield shift of signals due to the inner aryl protons (8- and 16-H) indicates the formation of a cyclophane structure. Table 2 shows chemical shifts for the inner aryl protons. Chemical-shift changes were observed for C-δH for both methoxy and methyl series depending on X in the other benzene ring. The changes are, however, quite small to serve as a measure of the transannular interaction.

TABLE 1

5,13-Disubstituted [2.2]metacyclophanes (3) and (4)

Compound	M.p. (°C)	Formula	Carbon (%) Calc.	Carbon (%) Found	Hydrogen (%) Calc.	Hydrogen (%) Found	Nitrogen (%) Calc.	Nitrogen (%) Found
(3b)	107—110	$C_{18}H_{20}O$	85.67	85.19	7.99	8.01		
(4b)	153—154	$C_{17}H_{17}Br$	67.77	67.54	5.65	5.81		
(4c)	167—167.5	$C_{18}H_{17}N$	87.41	87.90	6.93	7.16	5.66	5.59
(4d)	188.5—190	$C_{17}H_{17}NO_2$	76.38	76.42	6.41	6.45	5.24	5.37

TABLE 2

Inner aryl proton chemical shifts for (3) and (4) [a]

Compound	C-δH	C-δ'H
(3a)	4.10	4.10
(3b)	4.02	4.25
(4a)	4.15	4.15
(4b)	4.17	4.25
(4c)	4.20	4.36
(4d)	4.24	4.42

[a] Determined in $CDCl_3$ using $SiMe_4$ as reference and shown in p.p.m. All triplets. For designation of the inner aryl protons see formula (3).

Carbon-13 n.m.r. chemical shifts were determined in $CDCl_3$ using $SiMe_4$ as an internal reference by the pulse-Fourier transform technique. The assignment was aided by intensity considerations, off-resonance continuous-wave decoupling, and calculations using Woolfenden's additivity parameters.[17] Results are summarized in Table 3.

The chemical shifts for compound (2) were rigorously assigned.[7] Substituents caused chemical shift changes in an expected manner. With the dimethyl compound (4a), for example, the observed and the calculated values on introduction of methyl groups into (2) agreed to within 0.2 p.p.m.[7] Accordingly we assigned each carbon resonance for the rest of compounds by calculating the expected chemical shift upon the introduction of the substituent.

While the C-α, C-β, and C-γ resonances for (4a—d) were, as expected, quite similar, the inner aryl carbon resonance, C-δ, showed a shift depending on the substituent in the other ring (Figure 1, Table 3). The shift changes are attributable to the transannular effect. Similarly, C-δ resonances for methoxy-compounds (3a) and (3b) differ by 0.7 p.p.m., reflecting the effect of the substituent in the other ring.

Compared with simple arene model compounds the chemical shifts for inner aryl carbons, C-δ and C-δ', have been shown to be anomalous and shifted downfield by 6—8 p.p.m. These carbon resonances were easily recognized by observing residual coupling in the off-resonance continuous-wave decoupling spectrum since a

TABLE 3

Carbon-13 n.m.r. chemical shifts for (3) and (4)

Compound	Aromatic carbons								Me	CH$_2$	MeO	CN
	C-α	C-β	C-γ	C-δ	C-α′	C-β′	C-γ′	C-δ′				
(3a)	160.4	110.6	140.3	129.3	160.4	110.6	140.3	129.3		40.9	55.2	
(3b)	160.5	110.8	140.4	130.0	138.0	126.1	139.0	133.6	21.4	40.8, 41.2	55.3	
(4a)	137.8	125.7	138.7	133.9	137.8	125.7	138.7	133.9	21.3	40.7		
(4b)	138.5	126.2	138.5	134.1	121.9	128.1	140.8	135.4	21.4	40.7		
(4c)	138.2	126.4	138.2	134.2	111.7	128.9	139.5	140.6	21.4	40.3, 40.6		119.5
(4d)	138.2	126.4	138.2	134.4	148.4	120.4	139.7	142.3	21.4	40.3, 40.8		

[a] Determined in CDCl$_3$ using SiMe$_4$ as reference and shown in p.p.m. For designation of aromatic carbons, see formula (3).

TABLE 4

Downfield shift of inner aryl carbon resonances of (3) and and (4) relative to the corresponding arene model compounds.

Compound	Arene	δ_{arene} [b]	$\Delta\delta_{C\text{-}\delta}$
(3a)	5-Methoxy-*m*-xylene	122.4	6.8
(3b)	5-Methoxy-*m*-xylene	122.4	7.6
(4a)	Mesitylene	127.4	6.5
(4b)	Mesitylene	127.4	6.7
(4c)	Mesitylene	127.4	6.8
(4d)	Mesitylene	127.4	7.0
(3a)	5-Methoxy-*m*-xylene	122.4	6.8
(3b)	Mesitylene	127.4	6.2
(4a)	Mesitylene	127.4	6.5
(4b)	5-Bromo-*m*-xylene	128.6	6.8
(4c)	5-Cyano-*m*-xylene	134.5	6.1
(4d)	5-Nitro-*m*-xylene	136.4	5.9

[a] $\Delta\delta = \delta_{cyclophane} - \delta_{arene}$. [b] The chemical shift for C-2.

large chemical-shift difference existed between inner and outer aryl proton resonances. Table 4 shows the chemical-shift difference, $\Delta\delta = \delta_{cyclophane} - \delta_{arene}$, between the inner carbon resonances in (3) or (4) and the corresponding resonances for 5-substituted *m*-xylene or mesitylene. Not only carbon *para* to substituent X (C-δ′) but transannular carbon (C-δ) showed a substituent-dependent shift. As the substituent becomes more electron-withdrawing the C-δ′ resonance experiences less of a steric-compression shift while the C-δ resonance undergoes a further downfield shift. The results are rationalized by assuming an electron flow from the mesitylene ring to the substituted ring when the electron-withdrawing substituent is present. Both shift changes were found to be complementary as illustrated in Figure 1.

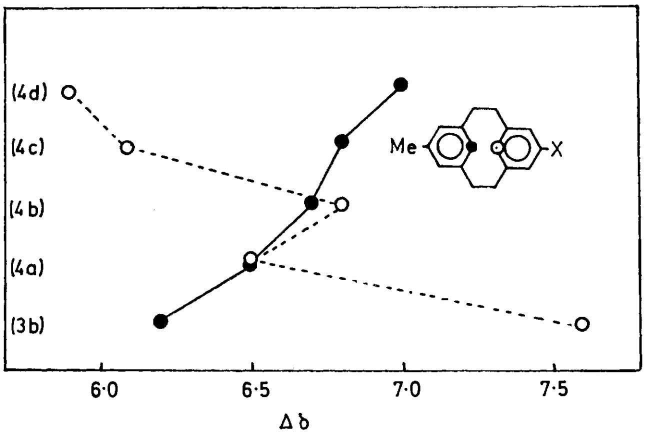


FIGURE 1 Chemical shift changes, $\Delta\delta = \delta_{cyclophane} - \delta_{arene}$, for the inner carbon resonances in (3b) and (4a)—(4d)

Cyclic Voltammetry.—Cyclic voltammetry was carried out in acetonitrile containing 0.1M of tetrabutylammonium perchlorate as a supporting electrolyte [1,13] and with a s.c.e. reference electrode; the voltammetry was carried out with a variety of scan rates. In Table 5 the peak potentials E_p at 250 mV^{-1} are summarized. The results for (4a) [13] are included for the purpose of comparison. Typical voltammograms are shown in Figure 2.

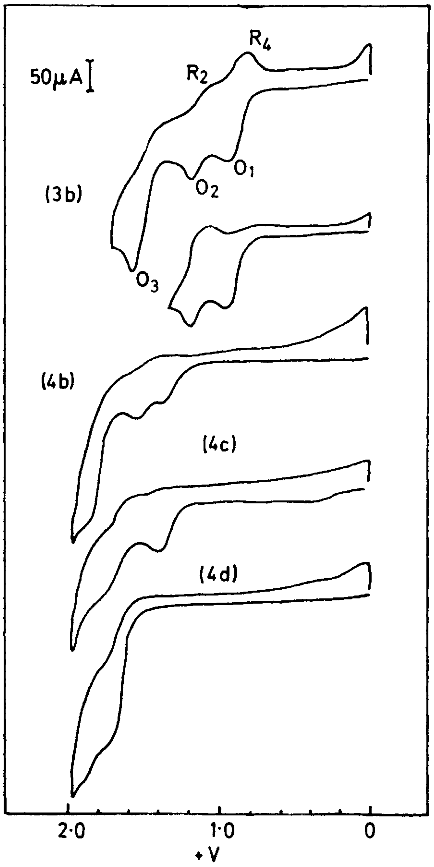


FIGURE 2 Cyclic voltammograms for (3b) and (4b)—(4d), determined in acetonitrile using Bu$^n{}_4$NClO$_4$ (0.1M) as supporting electrolyte at 250 mV s^{-1}, +V *vs.* s.c.e.

The first electron transfer is found to be irreversible, a feature characteristic of lower rates of electron transfer. The second anodic peak O$_2$ is accompanied by a peak R$_2$ on potential reversal and hence is a quasi-reversible electron-transfer stage. A high potential peak O_3 appeared as a shoulder for (4d). No peak O_3 was observed for (4c) in the potential range of 0—2.0 V.

Peak potentials for O_1, O_2, and O_3 showed successive anodic shifts as the substituent becomes more electronegative (Figure 2, Table 5). At higher scan rates O_1 showed a greater anodic shift compared with O_2 thus reflecting a slower electron transfer for the former. For the methoxy-compounds (3a) and (3b) a more detailed discussion is given below.

TABLE 5

Peak potentials E_p for (3) and (4), +V *vs.* s.c.e.[a]

Compound	Peak potential, E_p							Arene	E_p, O_1	ΔE_p, O_1
	O_1	O_2	O_3	O_4[b]	R_2	R_4	R_5			
(3a)	0.83	1.08	1.41	0.93	1.00	0.90	0.80	5-Methoxy-*m*-xylene	1.62	0.79
(3b)	0.95	1.17	1.57	0.95	1.10	0.86		5-Methoxy-*m*-xylene	1.62	0.67
(4a)	1.04	1.37	1.74		1.31			Mesitylene	2.03	0.99
(4b)	1.24	1.53	1.85		1.46			Mesitylene	2.03	0.79
(4c)	1.38	1.72			1.62			Mesitylene	2.03	0.65
(4d)	1.50	1.78						Mesitylene	2.03	0.53

[a] Determined in MeCN–$Bu^n_4NClO_4$ (0.1M) with substrate conc. 10^{-3}M. Scan rate 250 mV/s. Potential range 0 to +2.0 V. [b] Revealed by the potential-step sweep method. With (3b) O_4 overlapped completely with O_1 but could be identified by electrolysing the solution at the potential of O_1 which intensified O_4.

Figure 3 shows the relationship between O_1 and σ_p^+ both for the metacyclophanes (3) and (4) and also paracyclophanes.[1] Half-wave potential data are taken from the work of Shono *et al.*[18] Figure 4 shows the relation between E_p at O_1 and carbon-13 chemical shifts for the C-δ' resonances for compounds (4a)—(4d). On the basis of the E_p data electron abstraction is assumed to occur from the mesitylene ring. A linear correlation indicates that the electron-transfer rate is controlled by the substituent in the opposite ring as a result of the transannular effect.

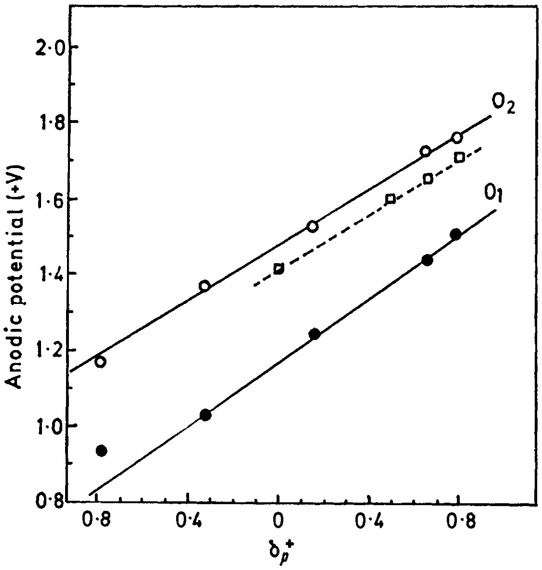


FIGURE 3 The relation between substituent constant and peak and half-wave potentials for [2.2]metacyclophane derivatives (3) and (4) (● O_1; ○ O_2) and [2.2]paracyclophane derivatives (□)

Half-wave potentials, $E_{1/2}$, were determined for representative compounds using a rotating platinum electrode; results for the first and second waves are shown in Table 6. These compounds showed three closely spaced oxidation plateaus which were separable only with difficulty. Comparison of $E_{1/2}$ (1) with E_p (O_1) revealed that the deviation was rather small, being 0.04 V for (4a) and 0.12 V for (4b).

Since the cyclic voltammetry (c.v.) method gave more reproducible results and since the deviation from $E_{1/2}$ values was at most 0.1 V at a slow scan rate we used E_p values for further comparisons.

Peak potential differences between those of cyclophanes and the corresponding arene model compounds equation (1), are shown in Table 5. It is largest for

$$\Delta E_p(O_1) = E_p(O_1)_{\text{arene}} - E_p(O_1)_{\text{cyclophane}} \quad (1)$$

(4a) and becomes smaller when an electron-withdrawing substituent is present. The smallest difference was observed for the nitro-compound (4d). The presence of a methoxy-group, (3a) and (3b), also caused a decrease in the peak potential difference compared with the dimethyl derivative (4a). The cathodic shift of 1 V found for (4a) is surprising since the fully overlapped

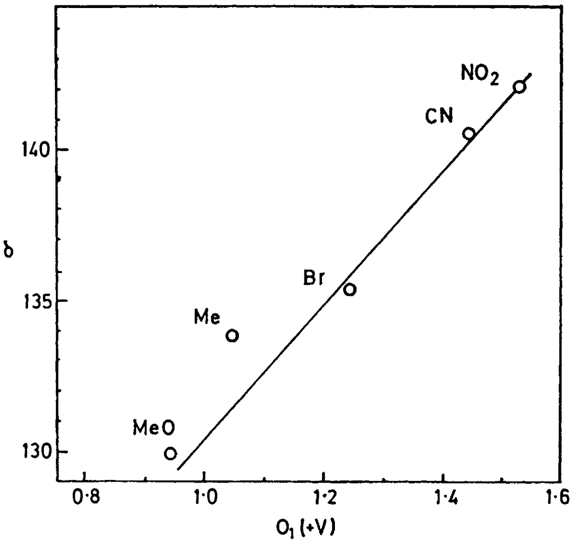


FIGURE 4 The relation between E_p (O_1) V *vs.* s.c.e., and C-13 n.m.r. chemical shift for the carbon resonance *para* to the substituent, δ for (3b) and δ' for (4a), (4b), (4c), and (4d)

paracyclophane (1) showed a cathodic shift of 0.5 V[1] compared with the E_p of *p*-xylene.

For all compounds except for the methoxy-compounds (3a) and (3b) reproducible voltammograms were recorded on repeated scans. Current decrease was much less compared with the unsubstituted compound (2). Thus 5,13-substituents in (4) were found to depress the intermolecular reaction expected when these positions were unblocked.[13]

TABLE 6

Half-wave potentials $E_{1/2}$ for (3) and (4), +V *vs.* s.c.e.[a]

Compound	$E_{1/2}$ (1)	$E_{1/2}$ (2)
(3b)	0.89	1.14
(4a)	1.08	1.38
(4b)	1.12	1.49
(4c)	1.28	1.71
(4d)	1.45	1.71

[a] Determined in MeCN–$Bu^n_4NClO_4$ (0.1M) using a rotating platinum electrode and polarography equipped with automatic potential controller.

The methoxy-compounds (3a) and (3b) showed remarkable voltammogram changes on repeated scans or scan rate changes. Table 7 shows scan-rate dependence of peak potentials O_1 and O_2 for (3a). The quasi-redox couple O_2–R_2 showed only a slight change for high speed scanning (achieved by storage of data using a wave-memory apparatus) compared with that carried out at a normal speed. The peak potential O_1, however, showed a progressive anodic shift indicative of slow electron transfer. As a result two waves merged at a higher scan rate (>7.5 V s^{-1}, Table 7).

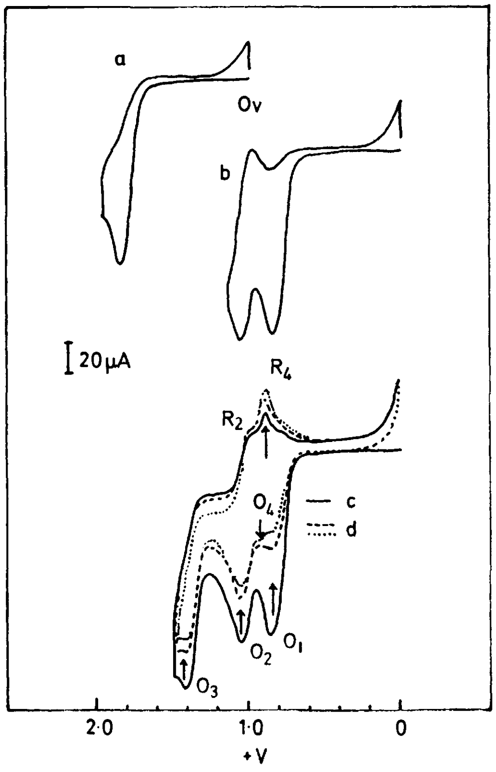


FIGURE 5 Wave-clipping experiments for (3a): a, 0 to +0.99 V; b, 0 to +1.15 V; c, 0 to +1.5 0V; d, second (— — —) and third (· · · ·) scans

Figure 5 shows the results of wave-clipping experiments. Whereas O_1 showed no corresponding R_1 peak when the potential was reversed at +0.99 V (curve a), the O_2–R_2 couple was clearly recorded by the scan between 0 to +1.15 V (curve b). When the scan was extended O_3 appeared at around +1.4 V. On potential reversal at +1.5 V R_3 appeared as a shoulder together with a new peak at +0.90 V (R_4, curve c). Depending on the conditions another cathodic wave was recorded at 0.80 V. Repeated scanning caused an increase in R_4 and a decrease in O_1 (curve d). A new peak at +0.93 V may be ascribed to the anodic peak corresponding to R_4 (O_4, curve d).

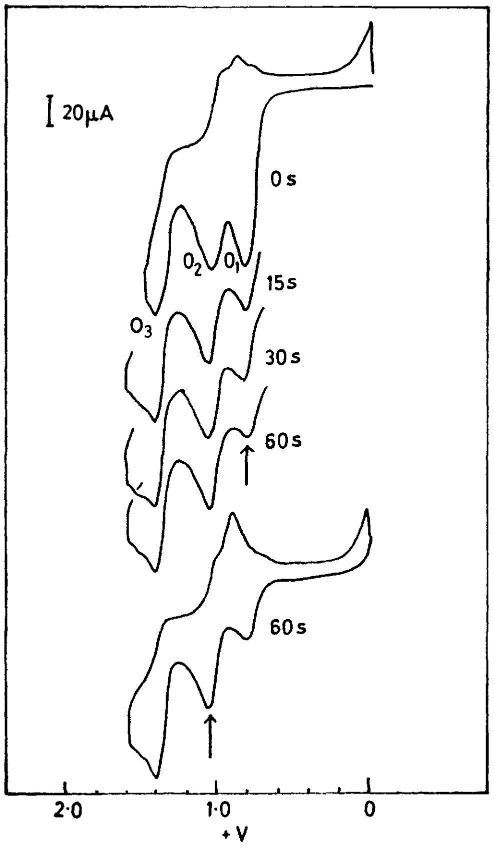


FIGURE 6 Cyclic voltammograms recorded after holding the potential at +0.8 V (E_p, O_1) and +1.0 V (E_p, O_2) for specified time at the potential of arrow (O_1 or O_2)

TABLE 7

Peak potentials E_p for (3a), +V *vs.* s.c.e.[a]

Scan rate, mV/s	E_p (O_1)	E_p (O_2)
100	0.82	1.05
250	0.86	1.06
500	0.89	1.06
750	0.86	1.06
1 000	0.93	1.10
1 250	0.94	1.09
3 000	1.05	1.15
5 000	1.05	1.15
7 500	1.15	1.18

[a] *Cf.* Table 5.

The potential-step sweep method was then carried out.[19] Figure 6 shows a successive decrease of O_1 is accompanied by an increase of O_2 and O_3 when the solution was electrolysed at 0.8 V (*ca.* E_p of O_1) for 15, 30, and 60 s. A c.v. curve recorded after the solution had been electrolysed at the potential of O_2 showed similar results (Figure 6). When the potential of O_3 was used (1.4 V) the O_4–R_4 couple increased and O_2 and O_3 decreased. The peak corresponding to O_1 disappeared completely after 30 s (Figure 7).

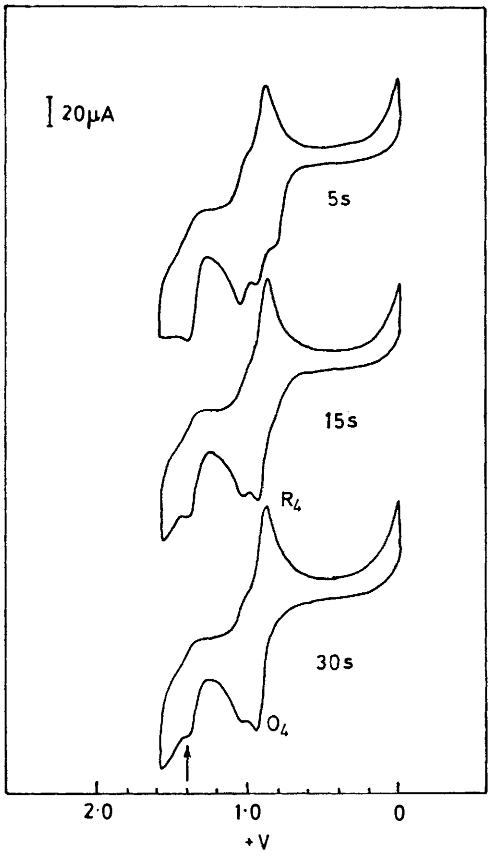


FIGURE 7 Cyclic voltammograms recorded after holding the potential at +1.40 V (E_p, O_3) for specified time

Transannular Dehydrogenation Reaction.—From the above results the first anodic wave for metacyclophanes was found to be highly dependent on the substituent in the opposite ring. It was also found that the first wave was irreversible and might involve a slower electron-transfer rate than the product wave O_2. Since the rate of the chemical reaction following the O_1 step would also be dependent on the nature of the substituent, the treatment remained qualitative and no further quantitative argument could be made.

We have reported[13] the formation of 2,7-dimethyl-4,5,9,10-tetrahydropyrene (5d) in a high yield by the anodic electrolysis of (4a) at +1.4 V, close to the potential of O_2 or the second half-wave potential $E_{1/2}(2)$ of (4a). Further dehydrogenation products, such as dimethyldihydropyrene and dimethylpyrene, were also noted. The parent hydrocarbon (2) gave (5a)[13] but the formation of polymeric products as a result of the reactivity of the unblocked 5,13-positions lowered the yield.

When the substituted compounds (3a), (3b), (4b), (4c), and (4d) were similarly electrolysed anodically at the potential of O_1 a very high yield of the corresponding compound (5) was obtained with the consumption of *ca.* 2 F mol^{-1} of electricity; the current efficiency was above 90%. No further dehydrogenation was observed unless a potential higher than that of O_1 was applied.

The peak potential data for (5) are shown in Table 8.

TABLE 8

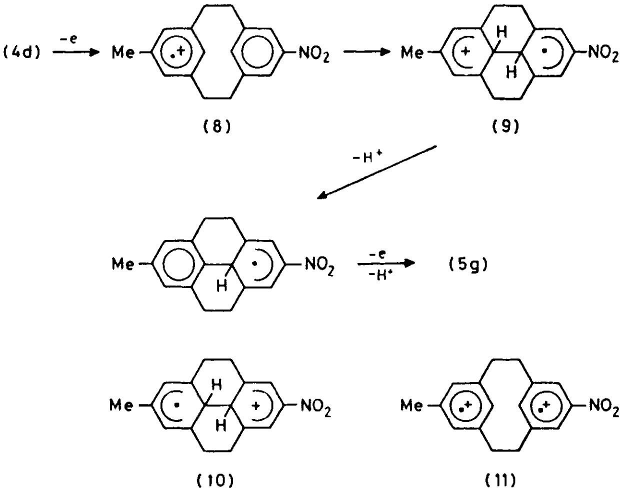
Peak potentials E_p for (5), +V *vs.* s.c.e.[a]

	Peak potential, E_p			
Compound	O_1	O_2	R_1	R_2
(5b)	1.05	1.40	0.95	1.32
(5c)	1.17		1.10	0.87
(5d)	1.40	1.90	1.32	
(5e)	1.53		1.45	
(5f)	1.73			
(5g)	1.74			

[a] *Cf.* Table 5.

It was soon found that O_2, O_3, and R_2 in (3) and (4) arise from the product (5) since they agreed with those of O_1, O_2, and R_1 of the latter.

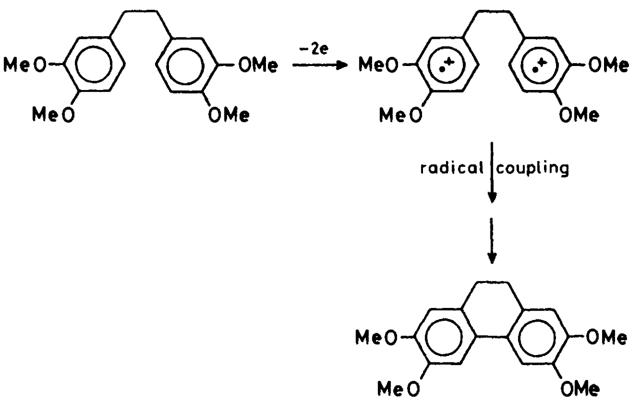
The anodic dehydrogenations of (3) and (4) were found to be quite general and proceeded very efficiently regardless of the nature of the substituent in one of the rings. The appearance of an R_4 peak for (3a) and (3b) might suggest the formation of an intermolecular coupling product[19] but attempted isolation failed since the reaction required a high potential which further oxidized any intermolecular product formed. Aryl coupling for cyano- and nitro-compounds requires radical attack to give the cation radical (9). Scheme 2 illustrates the possible course of the reaction taking the nitro-compound as an example. Electron abstraction at the potential of O_1 is assumed, on the basis of the half-wave potential data for substituted arenes,[20] to occur on the mesitylene side



SCHEME 2

of the ring. The cation radical (8) can attack the opposing arene either by electrophilic or radical species. Since the evidence available suggests that nitroarenes are easily arylated by aryl radical species [21] the coupling would be more likely to give the transannular cation radical (9) rather than the electrophilic reaction product (10). Further the CEC reaction of (9) gives (5g). Further, radical coupling of the bis-cation radical (11) is unlikely since the transannular reaction occurred at the potential of O_1. It is highly probable that the slow electron transfer at O_1 is concerted with transannular radical attack since. Otherwise the remarkable cathodic shift of O_1 for cyclophanes from that of simple arene model compounds cannot be explained.

It is interesting to compare the present findings with the formation of dihydrophenanthrene as shown in Scheme 3. For the aryl coupling reaction in acyclic compounds a bis-radical cation mechanism has been established on the basis of sound experimental evidence.



SCHEME 3

Recently, the bis-radical cation coupling mechanism was advanced for the formation of (5b) [22] but this is judged unlikely on the evidence of our extensive c.v. experiments.

EXPERIMENTAL

Measurements.—Proton and carbon-13 n.m.r. spectra were determined on a Hitachi R-20B or on a JEOL FX-60 spectrometer using $CDCl_3$ as solvent. The chemical shifts were given as δ values from $SiMe_4$. Electrochemical determinations were performed as previously reported.[1,13] A preparative controlled-potential anodic reaction was carried out as before.[13]

6-*Bromo*-15-*methyl*-2,11-*dithia*[3.3]*metacyclophane* (6; R = Br).—A solution of α,α′-dibromomesitylene [15] (1.9 g, 11 mmol) and sodium hydroxide (1.8 g, 45 mmol) in nitrogen-saturated 60% aqueous ethanol (200 ml) and a solution of 5,α,α′-tribromo-*m*-xylene [23] (3.8 g, 11 mmol) in benzene (200 ml) were added simultaneously over 5 h to a stirred solution of benzene (200 ml) and 95% ethanol (400 ml) in a Morton flask using a modified Hershberg funnel; the mixture was then refluxed and stirred overnight. Evaporation gave a solid which was extracted with dichloromethane and worked up as usual. Vacuum sublimation followed by recrystallization from chloroform–hexane gave 3.8 g (93%) of (6; R = Br) as colourless *prisms*, m.p. 123—124 °C; ^1H δ ($CDCl_3$) 7.00 (2 H), 6.90 (1 H), 6.80 (1 H), 6.72 (2 H), 3.75s (4 H), 3.72s (4 H), and 2.21s (3 H) (Found: C, 55.95; H, 4.7. $C_{17}H_{17}BrS_2$ requires C, 55.88; H, 4.69%).

Similarly other derivatives were prepared.

6-*Methoxy*-15-*methyl*-2,11-*dithia*[3.3]*metacyclophane* (6; R = OMe); colourless needles from ether–hexane, m.p. 123—124 °C; ^1H n.m.r. δ ($CDCl_3$) 6.73, 6.66, 6.48 (6 H), 3.71 (11 H), and 2.18 (s, 3 H) (Found: C, 68.45; H, 6.4. $C_{18}H_{20}OS_2$ requires C, 68.31; H, 6.37%).

6-*Methyl*-15-*nitro*-2,11-*dithia*[3.3]*metacyclophane* (6; R = NO_2); colourless prisms from benzene, m.p. 182—183 °C; ^1H n.m.r. δ ($CDCl_3$) 7.71 (2 H), 7.40 (t, 1 H), 6.95 (t, 1 H), 6.67 (2 H), 3.87 (s, 4 H), 3.80 (s, 4 H), and 2.03 (s, 3 H) (Found: C, 61.65; H, 5.2; N, 4.2. $C_{17}H_{17}NO_2S$ requires C, 61.60; H, 5.17; N, 4.23%).

6-*Cyano*-15-*methyl*-2,11-*dithia*[3.3]*metacyclophane* (6; R = CN); colourless prisms from chloroform–ether, m.p. 154.5—155.5 °C; ^1H n.m.r. δ ($CDCl_3$) 7.27 (t, 1 H), 7.15 (2 H), 6.88 (t, 1 H), 6.67 (2 H), 3.78 (s, 8 H), and 2.16 (s, 3 H) (Found: C, 69.15; H, 5.7; N, 4.4. $C_{18}H_{17}NS_2$ requires C, 69.41; H, 5.50; N, 4.50%).

6-*Cyano*-15-*methyl*-2,11-*dithia*-2,2,11,11-*tetraoxo*[3.3]*metacyclophane* (7; R = CN).—The bis-sulphide (6; R = CN) (1.5 g, 4.0 mmol) was dissolved in benzene (1 l) and glacial acetic acid (600 ml). To this solution 30% aqueous hydrogen peroxide (3 g) was added. After stirring for 24 h, hydrogen peroxide (3 g) was added and the stirring was continued for 48 h. Crystalline material separated and was collected to give the bis-sulphone (7; R = CN) (1.5 g, 83%), m.p. >300 °C; $\nu_{max.}$ (KBr) 2 230, 1 315, 1 295, and 1 110 cm^{-1}. This was used for pyrolysis without further purification.

Similarly other sulphones (7; R = MeO, Br, and NO_2) were prepared.

5-*Bromo*-13-*methyl*[2.2]*metacyclophane* (4b).—The bis-sulphone (7; R = Br) (200 mg, 0.47 mmol) was pyrolysed using a furnace similar to that described by Vögtle *et al.*[16] at 500 °C under reduced pressure. A pre-heater for sublimation was raised to 300 °C. Recrystallization of the sublimate gave 92 mg (65.6%) of (4b).

5-Methoxy-13-methyl- (3b), 5-cyano-13-methyl- (4c), and 5-methyl-13-nitro-[2.2]metacyclophanes (4d) were prepared similarly. Analytical and spectral data are collected in Tables 1—3.

5,13-Dimethoxy- (3a) [14] and 5,13-dimethyl-[2.2]metacyclophanes (4a) [15] were prepared according to the literature, m.p. (3a), 168—170 °C; (4a), 147—148 °C.

2,7-*Disubstituted*-4,5,9,10-*tetrahydropyrenes* (5b), (5c), (5e), (5f), *and* (5g).—Anodic oxidation of 5,13-disubstituted[2.2]-metacyclophane was carried out in acetonitrile containing 0.1M of $Bu^n{}_4NClO_4$ at the potential of O_1 using the method described previously.[1,13]

2-*Methoxy*-7-*methyl*-4,5,9,10-*tetrahydropyrene* (5c) was obtained when the electrolysis of (3b) was carried out at +0.90 V consuming 22.1 C of electricity where a two-electron process required 28.8 C, m.p. 121—122 °C; ^1H n.m.r. ($CDCl_3$) δ 6.89 (s, 2 H), 6.64 (s, 2 H), 3.82 (s, 3 H), 2.82 (s, 8 H), and 2.31 (s, 3 H) (Found: C, 86.4; H, 7.25. $C_{18}H_{18}O$ requires C, 86.36; H, 7.25%).

2,7-Dimethoxy-4,5,9,10-tetrahydropyrene (5b) obtained from (3a) agreed with that reported by Boelkelheide *et al.*[14]

2-*Bromo*-7-*methyl*-4,5,9,10-*tetrahydropyrene* (5e), m.p. 160—161 °C; ^1H n.m.r. ($CDCl_3$) δ 7.17 (s, 2 H), 6.86 (s, 2 H, 2.80 (s, 8 H), and 2.28 (s, 3 H); *m/e* M^+ 298 and 300 (Found: C, 68.25; H, 5.15. $C_{17}H_{15}Br$ requires C, 68.24; H, 5.05%).

2-*Cyano*-7-*methyl*-4,5,9,10-*tetrahydropyrene* (5f), m.p. 179—180 °C, ^1H n.m.r. ($CDCl_3$) δ 7.33 (s, 2 H), 6.94 (s, 2 H), 2.86 (s, 8 H), and 2.34 (s, 3 H); *m/e* M^+ 245 (Found: C, 87.95; H, 6.2; N, 5.65. $C_{18}H_{15}N$ requires C, 88.13; H, 6.16; N, 5.71%).

2-*Methyl*-7-*nitro*-4,5,9,10-*tetrahydropyrene* (5g), m.p. 158—159.5 °C; ^1H n.m.r. ($CDCl_3$) δ 7.95 (s, 2 H), 6.97 (s, 2 H), 2.93 (s, 8 H), and 2.36 (s, 3 H); *m/e* 265 (Found: C, 76.55; H, 5.65; N, 5.15. $C_{17}H_{15}NO_2$ requires C, 76.96; H, 5.70; N, 5.28%).

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