

## Electro-organic Chemistry. Part 2.<sup>1</sup> Structure and Anodic Peak Potential Relationships. Cyclophanes. Cyclic Voltammetric Studies of Cation-radical Formation and Reactions

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The peak potentials for a series of cyclophanes were measured and compared with those of model compounds. Measurements were performed by cyclic voltammetry in acetonitrile-tetrabutylammonium perchlorate. Cyclic voltammetry revealed that the first electron-transfer step was not reversible and that the rate of electron transfer dominated. Peak potentials measured at 250 mV s<sup>-1</sup> were used for comparison. Compared with xylene the anodic peak potentials were lowered as follows: [2.2]meta- ( $\Delta O_1$  0.75 V), [2.2]para- (0.51 V), and [2.2]meta-para-cyclophanes (0.29 V). Electron-withdrawing substituents increased the potential of one-electron abstraction from the opposite benzene ring for [2.2]para- and [2.2]metapara-cyclophane reflecting  $\pi$ - $\pi$  interactions. 5,13-Dialkyl[2.2]metacyclophane had an anomalously low peak potential with  $\Delta O_1$  almost 1 V. Other dialkyl derivatives showed no such anomaly indicating the dependence on the position of substitution. Homologous compounds were found to be less anomalous. The geometrical isomers of [2.2] (2,7)naphthalenophane behaved differently and the *trans*-isomer showed two oxidation peaks instead of one with lower  $O_1$  than for the *cis*-isomer. The possible involvement of a transannular cation-radical from [2.2]metacyclophane is suggested for electrophilic and photolytic reactions as well as for reactions with metal salts.

RECENTLY, one electron-transfer processes have been recognized as essential steps not only for the generation and interconversion of various reactive intermediates<sup>2</sup> but also in a number of bio-organic redox reactions.<sup>3</sup> The course of reactions is highly dependent on reduction-oxidation potentials as well as a number of other variables. Indeed, intervention of an electron-transfer process has been reported even in cases where the mechanism had seemingly been established.<sup>4</sup>

To gain a better understanding of the relation between structure and oxidation potential we have carried out electrochemical measurements on cyclophane compounds. These compounds were selected for the following reasons. (1) Cyclophanes are unique in having two aryl or other  $\pi$  systems in extreme proximity. We wished to know how this proximity effect and the strain energy term affected the ease of electron transfer. Also interesting is the fate of a cation-radical formed in a strained molecular framework. (2) Recently, the anion-radical of cyclophanes formed by alkali metal reduction have been investigated by e.s.r. and ENDOR.<sup>5-11</sup> These studies revealed the dependence of  $\pi$  spin delocalization on the length of the methylene bridges in [*m.n*]paracyclophanes.<sup>5-8</sup> Metacyclophanes and naphthalenophanes have been shown to undergo dehydrogenation, cleavage, and also deep seated rearrangements.<sup>9-11</sup>

### METHODS

Peak potentials were determined in acetonitrile containing 0.1M-tetrabutylammonium perchlorate (TBAP) at 25 °C

<sup>1</sup> Part I, T. Sato and M. Kamada, *J.C.S. Perkin II*, 1977, 384.

<sup>2</sup> S. P. McManus, 'Organic Reactive Intermediates,' Academic Press, New York, 1973.

<sup>3</sup> L. Stryer, 'Biochemistry,' Freeman, San Francisco, 1975, p. 331; D. Dolphin and R. H. Felton, *Accounts Chem. Res.*, 1974, 7, 26; U. Eisner and J. Kutman, *Chem. Rev.*, 1972, 72, 1; A. Ohno, T. Kimura, H. Yamamoto, S. G. Kim, S. Oka, and Y. Ohnishi, *Bull. Chem. Soc. Japan*, 1977, 50, 1535, 2385.

<sup>4</sup> K. A. Bilevitch, N. N. Pubnov, and O. Yu. Okhobystin, *Tetrahedron Letters*, 1968, 3465; S. Bank and K. A. Noyd, *J. Amer. Chem. Soc.*, 1973, 95, 8203; N. Kornblum, R. E. Michel, and R. C. Kerber, *ibid.*, 1966, 88, 5662; G. A. Russel and W. C. Danen, *ibid.*, p. 5663.

using the s.c.e. as reference. Trifluoroacetic acid-methylene chloride was also used as solvent. Substrate concentrations were of the order of 10<sup>-3</sup>M.

The half-wave potential  $E_{1/2}$  was determined by a Shimadzu RP-50 polarograph equipped with an AIC-50 automatic potential corrector using an RE-50 rotating platinum electrode. Cyclic voltammetry was carried out using a Hokuto HA-107A function generator and a Hokuto HB-101 potentiostat. Scan rates ranged from 0.05 to 50 V s<sup>-1</sup>. For high speed cyclic voltammetry an NF WM-812A circuit block wave-memory unit was connected for time scale conversion. Each measurement was performed at at least three scan speeds, 100, 250, and 500 mV s<sup>-1</sup>. A Beckman No. 39273 platinum inlay electrode was used as anode and platinum wire as cathode. The cell used for both measurements was similar to that described previously.<sup>1</sup>

The first-electron-transfer step for compounds here examined showed no reversible redox behaviour and the rate of electron transfer was dominant. The peak potential became more anodic when faster scan rates were used.

Polarographic determinations were carried out for representative compounds and data are shown in Tables 1 and 2. Compared with the half-wave potentials  $E_{1/2}$  peak potentials tend to be more anodic but the difference is only slight when the scan rate is low. Since it is not easy to determine  $E^0$  we attempted to use peak potentials at 250 mV s<sup>-1</sup> for comparison purposes. It is true that the peak potential is not only related to the stability of the cation-radical but to the rate for the following fast reaction. The present treatment is thus qualitative in nature.

Cyclic voltammetry is not only an efficient and convenient

<sup>5</sup> A. Ishitani and S. Nagakura, *Mol. Phys.*, 1967, 12, 1.

<sup>6</sup> F. Gerson and W. B. Martin, jun., *J. Amer. Chem. Soc.*, 1969, 91, 1883.

<sup>7</sup> J. M. Pearson, D. W. Williams, and M. Levy, *J. Amer. Chem. Soc.*, 1971, 93, 5478.

<sup>8</sup> F. Gerson, W. B. Martin, jun., and Ch. Wydler, *J. Amer. Chem. Soc.*, 1976, 98, 1318.

<sup>9</sup> H. Kowata, M. Hoshino, and M. Koizumi, Abstracts 24th Annual Meeting of the Chemical Society of Japan, Osaka, 1971.

<sup>10</sup> Ch. Elschenbroich, F. Gerson, and V. Boekelheide, *Helv. Chim. Acta*, 1975, 58, 1245.

<sup>11</sup> Ch. Elschenbroich, F. Gerson, and J. A. Reiss, *J. Amer. Chem. Soc.*, 1977, 99, 60.

way of determining anodic potentials but it possesses a number of merits over polarography.<sup>12</sup> Multi-oxidation peaks are cleanly separated, electron transfers can be studied in more detail utilizing a large time scale, and high potential waves can be readily assigned due to clear peak formation.

## RESULTS

Representative voltammograms are shown in Figures 1—3. Peak potentials from the cyclic voltammetric measurements and half-wave potentials are summarised in Tables 1 and 2 ( $E_{1/2}$  values in parentheses).

*Paracyclophanes and Related Compounds.*—The half-wave potential of [2.2]paracyclophane (1a) is 1.52 V versus s.c.e.

metry was carried out in  $\text{CF}_3\text{COOH}-\text{CH}_2\text{Cl}_2$  (1:4),  $\text{O}_1$  appeared at 1.28 V with a cathodic shift of ca. 0.23 V. Not much shift was observed for  $\text{O}_2$  as seen from Figure 1. Aryl cation-radicals are reported to be stabilized in  $\text{CF}_3\text{COOH}-\text{CH}_2\text{Cl}_2$ .<sup>13</sup>

The open chain models, 4,4'-dimethyl- and -diethyl-bibenzyl (2) or *p*-xylene undergo electron transfer at the anode at ca. 2 V. Compared with these compounds the lowering of the peak potential for (1a) reached ca. 0.5 V. That this is caused by  $\pi$  assistance from the facing benzene ring is readily shown from the observations for the mono-substituted derivatives (1b),<sup>14</sup> (1c),<sup>15</sup> and (1d)<sup>15</sup> in which the peak potential is found to be dependent on the electronic

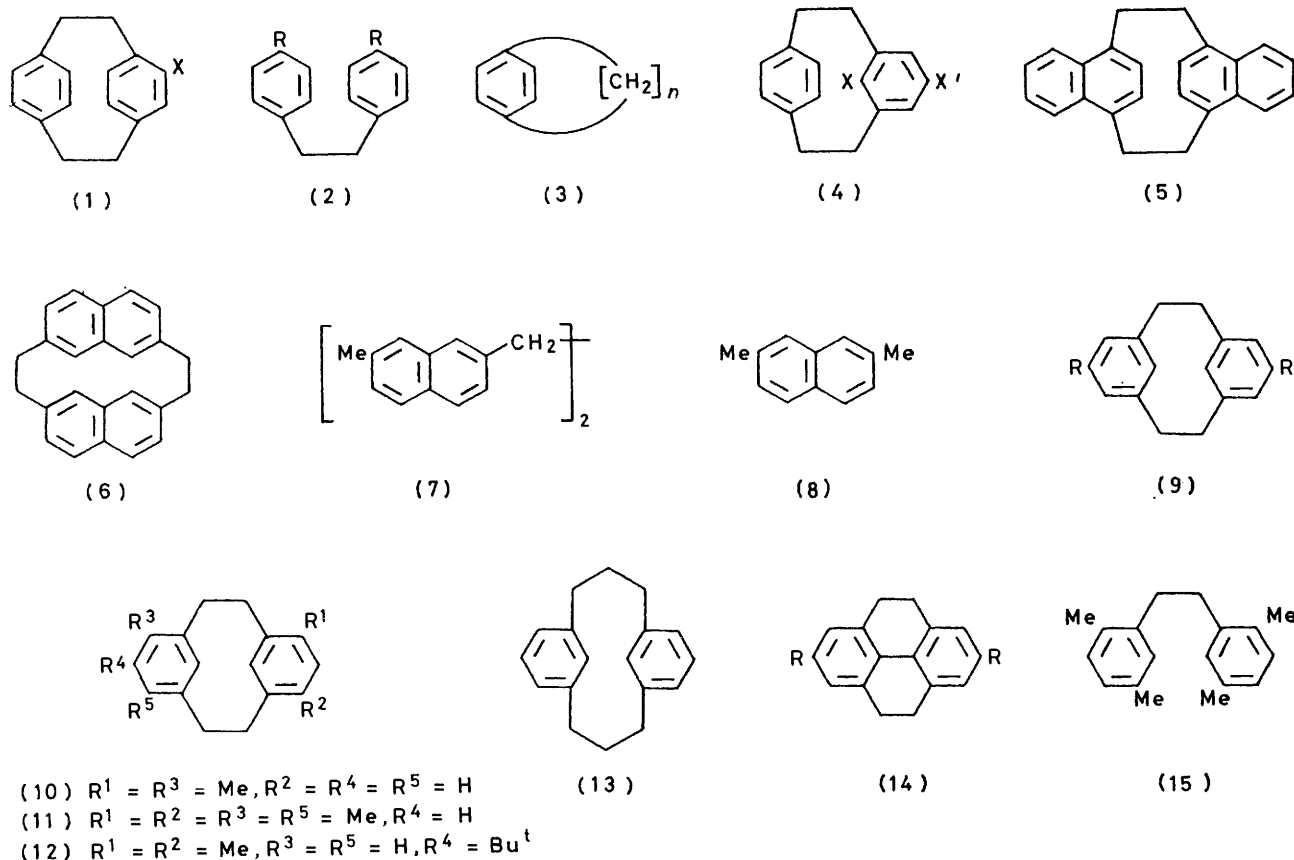


Figure 1 shows the voltammogram for (1a). At the scan rate of  $250 \text{ mV s}^{-1}$  two anodic peaks,  $\text{O}_1$  and  $\text{O}_2$ , were recorded at 1.57 and 1.80 V respectively. The  $\text{O}_1$  value is slightly higher than  $E_{1/2}$  as expected but the difference is quite small (0.05 V).  $\text{O}_2$  corresponds to a second electron transfer from the other benzene ring.

The peak potential varies with the scan rate;  $\text{O}_1$  occurs at 1.51 and 1.72 V at scan rates of 100 and  $6000 \text{ mV s}^{-1}$  respectively. This is the result of slow electron transfer and a coupled fast chemical reaction. When cyclic voltam-

\* Prepared by Mr. T. Takemura. Details will be reported elsewhere.

<sup>12</sup> D. T. Sawyer and J. L. Roberts, jun., 'Experimental Electrochemistry,' Wiley, New York, 1974; B. E. Conway and E. J. Rudd, in 'Technique of Electroorganic Synthesis,' ed. N. L. Weinberg, New York, 1974, p. 149.

<sup>13</sup> K. Bechgaard, O. Hammerich, N. S. Moe, A. Ronlan, U. Svanholm, and V. D. Parker, *Tetrahedron Letters*, 1972, 2271.

<sup>14</sup> H. J. Reich and D. J. Cram, *J. Amer. Chem. Soc.*, 1969, **91**, 3545.

effect of the second ring which carries the electronegative substituent.

Recently, Shono and his co-workers<sup>16</sup> also examined  $E_{1/2}$  for a series of monosubstituted [2.2]paracyclophanes and observed a good linear correlation between  $E_{1/2}$  and Hammett's  $\sigma_p^+$  values.

The peak potentials for the [n]paracyclophanes (3) showed no such anomalous cathodic shift as observed for (1). [8]-,<sup>17</sup> [9]-,<sup>18</sup> and [11]-paracyclophanes\* exhibited  $\text{O}_1$  at ca. 2 V. The angle strain term appears to be less sensitive towards one-electron oxidation.

<sup>15</sup> D. J. Cram and N. L. Allinger, *J. Amer. Chem. Soc.*, 1955, **77**, 6289.

<sup>16</sup> T. Shono, A. Ikeda, J. Hayashi, and S. Hakozaiki, *J. Amer. Chem. Soc.*, 1975, **97**, 4261.

<sup>17</sup> D. J. Cram, C. S. Montgomery, and G. R. Knox, *J. Amer. Chem. Soc.*, 1966, **88**, 515.

<sup>18</sup> D. J. Cram and M. F. Antar, *J. Amer. Chem. Soc.*, 1958, **80**, 3109.

*Metaparacyclophanes* (4).—[2.2]Metaparacyclophane (4b) showed  $O_1$  at 1.79 V which is only slightly more cathodic than

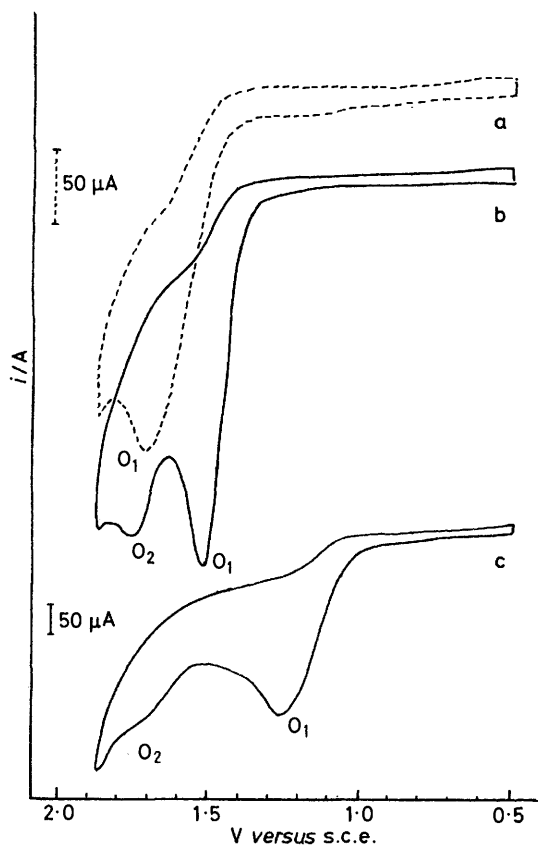


FIGURE 1 Scan rate and solvent dependence of the cyclic voltammograms of [2.2]paracyclophane (1a): a, at 6 000  $\text{mV s}^{-1}$  in MeCN-TBAP (0.1M); b, at 300  $\text{mV s}^{-1}$  in MeCN-TBAP (0.1M); and c, at 300  $\text{mV s}^{-1}$  in  $\text{CF}_3\text{CO}_2\text{H}-\text{CH}_2\text{Cl}_2$  (1:4) containing TBAP (0.1M)

the values for model compounds. Compared with the para compound (1a) less  $\pi-\pi$  interaction is expected between the two aryl rings since they are not parallel but inclined.<sup>19</sup>

The methoxy derivative (4a) \* showed  $O_1$  at 1.56 V, electron abstraction taking place from the methoxy-substituted ring. This value is to be expected for a methoxy-arene. Peak potentials for the bromo and nitro derivatives, (4c)<sup>20</sup> and (4d) † are also dependent on the substituent as in the case of (1) and the presence of an electron-withdrawing group raises the oxidation potential of the opposite benzene ring. For the isomeric nitro compounds (4d and e), in which the position of the nitro group is different, quite similar  $O_1$  values were found (Table 1).

*Naphthalenophanes*.—*anti*-[2.2](1,4)Naphthalenophane (5)<sup>21</sup> showed  $O_1$  at the very low potential of 1.07 V, indicative of a transannular stabilization effect. It also showed  $O_2$  and  $O_3$  peaks at the relatively low potentials 1.31 and 1.57 V, respectively.

\* See note on p. 1200.

<sup>19</sup> D. J. Cram and J. M. Cram, *Accounts Chem. Res.*, 1971, **4**, 204.

<sup>20</sup> S. A. Sherrod, R. L. da Costa, R. A. Barnes, and V. Boekelheide, *J. Amer. Chem. Soc.*, 1974, **96**, 1565.

<sup>21</sup> G. W. Brown and F. Sondheimer, *J. Amer. Chem. Soc.*, 1967, **89**, 7116.

<sup>22</sup> T. Sato, H. Matsui, and R. Komaki, *J.C.S. Perkin I*, 1976, 2051.

We found that the oxidation potential is further dependent on slight geometrical changes. Of the two isomeric naphthalenophanes (6)<sup>22</sup> the *trans* isomer showed an appreciably lower  $O_1$  (1.39 V) than the *cis*-isomer (1.65 V). The peak potential for the *cis*-compound is not much different from that of 2,7-dimethylnaphthalene (8). Moreover, the *trans*-isomer showed  $O_2$  following closely on  $O_1$ . Figure 2 shows the cyclic voltammograms for the isomers (6) and dimethylnaphthalene (8). Bis-(7-methyl-2-naphthyl)ethane (7) showed  $O_1$  at 1.54 V which is slightly lower than that of (8) indicating intramolecular cation-radical stabilization between two naphthalene groups.

Recently, Gerson and his co-workers<sup>11</sup> observed the cleavage of the *trans*-isomer of (6) into an anion-radical of (8) on long contact with alkali metal. The e.s.r. spectrum of the *trans*-compound could only be measured after short contact with a potassium mirror in dimethoxyethane.

*Metacyclophanes*.—The results for [2.2]metacyclophanes

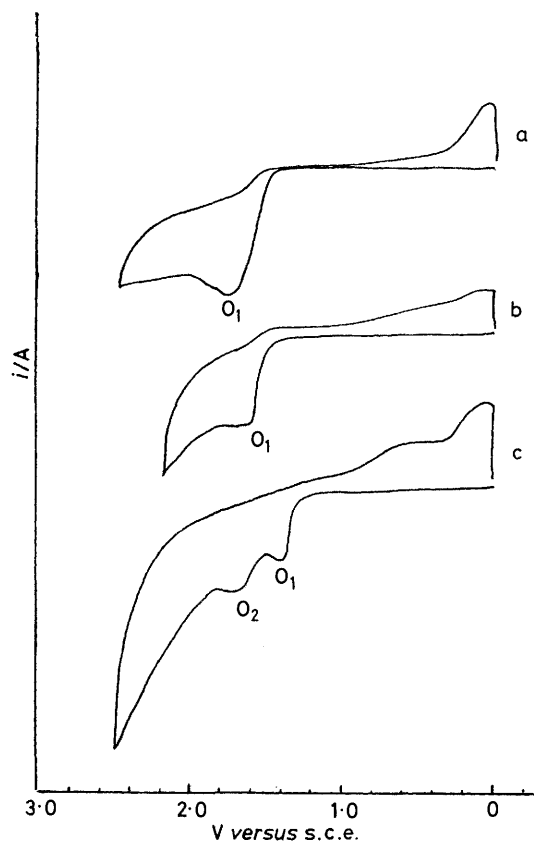


FIGURE 2 Cyclic voltammograms determined in MeCN-TBAP (0.1M) at 500  $\text{mV s}^{-1}$  of: a, 2,7-dimethylnaphthalene (8); b, *cis*-[2.2](2,7)naphthalenophane (6); and c, *trans*-(6)

(9a), (9b),<sup>23</sup> (9c),<sup>24</sup> (9d), (10),<sup>25</sup> (11),<sup>23</sup> and (12), [3.3]metacyclophane (13),<sup>26</sup> and the acyclic model (15) are summarized in Table 2. Compounds (9d) and (12) were prepared by methods described previously.<sup>23</sup>

<sup>23</sup> T. Sato, S. Akabori, S. Muto, and K. Hata, *Tetrahedron*, 1968, **24**, 5557.

<sup>24</sup> K. Nishiyama, K. Hata, and T. Sato, *J.C.S. Perkin II*, 1974, 577.

<sup>25</sup> T. Sato, S. Akabori, M. Kainosho, and K. Hata, *Bull. Chem. Soc. Japan*, 1968, **41**, 218; *J. Org. Chem.*, 1972, **37**, 3254.

<sup>26</sup> T. Shimoyozu, T. Inazu, and T. Yoshino, *Chemistry Letters*, 1976, 1405.

[2.2]Metacyclophanes were found to possess three characteristics not observed for other cyclophanes. (1) They exhibited the lowest  $O_1$  compared not only with the

TABLE 1

Peak potentials for para- and metapara-cyclophanes and naphthalenophanes<sup>a</sup>

Compound	Potential (V versus s.c.e.) <sup>a</sup>		
	$O_1$	$O_2$	$O_3$
(1a) X = H	1.57 (1.52)	1.80	
(1b) X = Br	(1.58)		
(1c) X = COCH <sub>3</sub>	1.66	1.90sh	
(1d) X = NO <sub>2</sub>	1.81		
(2; R = CH <sub>3</sub> )	2.05		
(2; R = C <sub>2</sub> H <sub>5</sub> )	2.06		
(3; n = 8)	1.96		
(3; n = 9)	1.99	2.32sh	
(3; n = 11)	1.97	2.41sh	
(4a) X = CH <sub>3</sub> O, X' = H	1.56	2.08	
(4b) X = X' = H	1.79		
(4c) X = Br, X' = H	1.78		
(4d) X = NO <sub>2</sub> , X' = H	1.86		
(4e) X = H, X' = NO <sub>2</sub>	1.87		
anti-(5)	1.07	1.31	1.57sh
trans-(6)	1.39	1.67	
cis-(6)	1.65		
(7)	1.54		
(8)	1.74		

<sup>a</sup> Determined in acetonitrile-tetrabutylammonium perchlorate (0.1M) at 250 mV s<sup>-1</sup>.  $E_{1/2}$  values determined by using polarography with rotating platinum electrode are shown in parentheses. Potential range is 0–2.5 V. Concentration of the solution is of the order of 10<sup>-3</sup>M. For (5) a saturated solution was used. Shoulder is denoted as sh.

TABLE 2

Peak potentials for metacyclophanes and related compounds<sup>a</sup>

Compound	Potential (V versus s.c.e.)			
	$O_1$	$O_2$	$R_2$	$O_3$
(9a) R = H	1.41 (1.29)	1.69sh		1.87
(9b) R = CH <sub>3</sub>	1.04 (1.08)	1.37 (1.38)	1.31	1.74
(9c) R = C <sub>2</sub> H <sub>5</sub>	1.07	1.37	1.31	1.76
(9d) R = Bu <sup>t</sup>	1.08 (1.10)	1.39 (1.40)	1.32	1.82sh
(10)	1.34	1.52sh		1.65 1.86sh (O <sub>4</sub> )
(11)	1.24	1.43		1.83
(12)	1.22	1.42		1.90
(13)	1.83			
(14a) R = H	1.66sh	1.85		
(14b) R = CH <sub>3</sub>	1.40	1.90sh	1.32 (R <sub>1</sub> )	
(14c) R = Bu <sup>t</sup>	1.40	1.82sh	1.32 (R <sub>1</sub> )	
(15)	2.06			

<sup>a</sup> See footnote to Table 1.

para and metapara counterparts but with homologous and other related compounds. (2) The first peak potential was found to be highly dependent on the presence and position of

\* Data for (9a–c) and (11) have been reported earlier.<sup>1</sup> On redetermination using an improved method we obtained good agreement between two measurements for the cyclic voltammetric data. We found, however, that the data obtained by using a rotating platinum electrode need revision. Ref. 1 gives  $E_{1/2}$  corresponding to the second wave. This time we obtained a good separation between  $E_{1/2}^1$  and  $E_{1/2}^2$  using a modification which permitted higher resolution of multi-stepped waves.

alkyl groups. (3) In the cyclic voltammogram there appeared at least three oxidation peaks in the range of 0–+2.0 V, showing  $O_1$  and  $O_2$  as closely spaced peaks.\* For comparison, Table 2 contains the half-wave potentials for the first and second waves.

[2.2]Metacyclophane (9a) showed  $O_1$  at 1.41 V which is lower than that of *m*-xylene ( $O_1$  2.16 V) by 0.75 V. It is a striking fact that compound (8a) is more susceptible to one-electron oxidation than the corresponding biphenyl model (14a), which had  $O_1$  at 1.66 V. Compound (9a) showed  $O_2$  and  $O_3$  at 1.69 and 1.87 V. These arise from the formation of the dehydrogenation product (14a). The rapid current

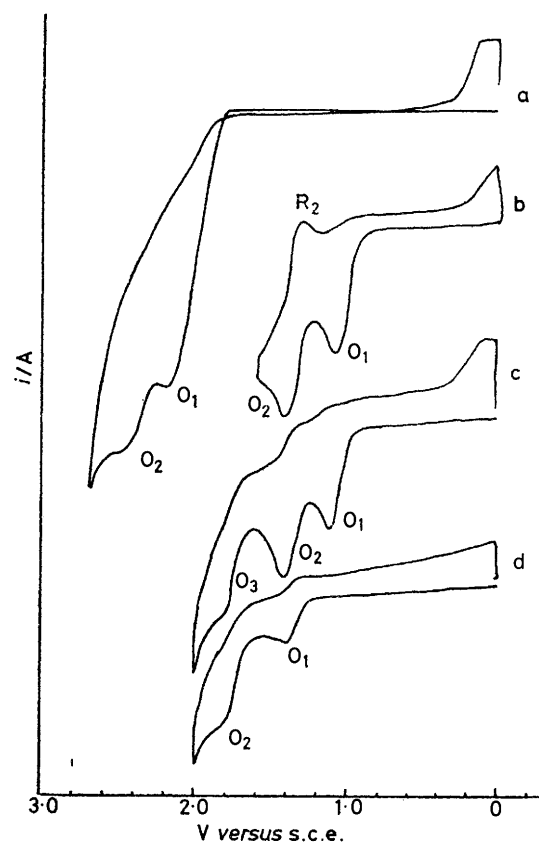


FIGURE 3 Cyclic voltammograms determined in MeCN-TBAP (0.1M) at 250 mV s<sup>-1</sup> of: a, 5-*t*-butyl-*m*-xylene; b, 5,13-di-*t*-butyl[2.2]metacyclophane (9d) with potential clipped at +1.60 V; c, (9d) with potential ranging between 0 and +2.0 V; and d, 2,7-di-*t*-butyl-4,5,9,10-tetrahydropyrene (14c)

decrease observed for (9a) upon repeated scans is due to the high reactivity of the 5- and 13-positions. No such current decrease occurred when these positions were blocked.

The 5,13-dimethyl derivative (9b) showed  $O_1$  more cathodic than that for mesitylene ( $O_1$  2.03 V) by almost 1 V. Unlike (9a)  $R_2$  appeared on potential reversal. The quasi-reversible couple  $O_2$ – $R_2$  became more distinct when the potential was clipped at 1.5 V. That this couple corresponded to the formation of (14b) was confirmed by controlled potential electrolysis.<sup>1</sup>

The isomeric dimethyl compound (10) showed  $O_1$  at 1.34 V which is close to that of unsubstituted (9a) but is appreciably more anodic than for (9b). In comparison, the open-chain model (15) showed  $O_1$  at 2.06 V. Further, the tetramethyl derivative (11) is oxidized at a higher potential than

that of (9b). In the benzene series, durene ( $O_1$  1.78 V), a model for (11), shows an appreciably lower  $O_1$  than does mesitylene, a model for (9b).

These results indicate the stabilizing effect exerted by 5,13-dimethyl groups on cyclophane cation-radical formation. Accordingly we determined the cyclic voltammograms for the ethyl and *t*-butyl compounds (9c and d). As Table 2 shows these are very similar to that of (9a).

Figure 3 shows the voltammograms for (9d), (14c), and 5-*t*-butyl-*m*-xylene. It was confirmed by controlled potential electrolysis of (9d) that at the  $O_1$  potential (14c) was formed in quantitative yield. Thus, again, the  $O_2$ - $R_2$  couple is due to formation of (14c) upon anodic oxidation at  $O_1$ .

The trisubstituted derivative (12) showed  $O_1$  almost equal to that of the tetramethyl compound (11) indicating that electron abstraction occurred from the durene ring. Both 5- and 13-alkyl groups appear to be necessary to lower the peak potential.

The higher homologue (13) showed  $O_1$  at 1.83 V with no  $O_2$  peak following closely after  $O_1$ , indicating the absence of transannular interaction.

## DISCUSSION

Of the three [2.2]cyclophanes, [2.2]paracyclophane (1a) is most strained and the excess enthalpy compared with two molecules of *p*-xylene is 31.5 kcal mol<sup>-1</sup> which is almost equal to that of cyclopropane.<sup>19,27</sup> The meta compound (9) is least strained and the excess energy of the metapara compound lies in between. The excess energy is due to extreme *p*-orbital compression which results in distortion of the benzene rings, bond angles, and bond lengths. A number of anomalous properties and reactions are attributable to this strain.<sup>19,28</sup>

The present survey on the peak potential-structure relationship revealed that the strain energy term alone is not the controlling factor but that the geometry of the molecule, especially the relative positions of two aromatic nuclei, is also important.

For transannular  $\pi$  assistance fully overlapped paracyclophanes, such as (1a) and (5), showed larger cathodic shifts compared with simple arene model compounds. [2.2]Metaparacyclophane (4b), on the other hand, showed a cathodic shift of only *ca.* 0.3 V. In (4b) the two benzene rings are inclined and the inner aryl position of the meta ring is directed towards the electron cloud of the para ring.

Substituent effects for [2.2]metaparacyclophane are much smaller than for (1a) reflecting less  $\pi$  assistance in the former. For example a nitro group shifted the potentials by 0.24 and *ca.* 0.08 V, respectively, for (1a) and (4b). The position of the nitro group in (4b) did not cause any difference [*cf.* (4d and e)].

The peak potentials are very cathodic in the highly reactive [2.2]metacyclophanes and related systems in which the two aryl rings are arranged in a stepped manner in parallel planes. For (9a) the peak potential was

found to be highly dependent on the number and position of alkyl groups. The *cis*-isomer of (6) shows higher anodic peak potential than the *trans*-isomer since it exists in a folded form. The extent of cathodic shift for representative cyclophanes is in the order: (9b), (9d) > (9a) > (1a), (10), (11), (12) > (4b), (13), *trans*-(6) > *cis*-(6) (Table 3). For the [2.2]para and [2.2]metapara

TABLE 3

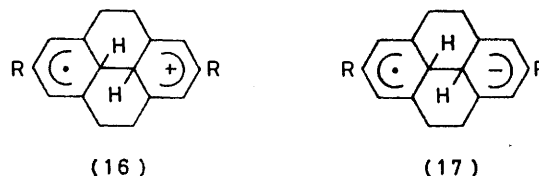
Comparison of the first peak potentials for cyclophane compounds and component arene models<sup>a</sup>

Cyclophane	$O_1/V$	Arene model	$O_1/V$	$\Delta O_1/V$
(1a)	1.57	<i>p</i> -Xylene	2.08	0.51
(4b)	1.79	<i>p</i> -Xylene	2.08	0.29
(9a)	1.41	<i>m</i> -Xylene	2.16	0.75
(9b)	1.04	Mesitylene	2.03	0.99
(9d)	1.08	5- <i>t</i> -Butyl- <i>m</i> -xylene	2.06	0.98
(10)	1.34	Pseudocumene	1.90	0.56
(11)	1.24	Durene	1.78	0.54
(12)	1.22	Durene	1.78	0.56
(13)	1.83	<i>m</i> -Xylene	2.16	0.33
<i>trans</i> -(6)	1.39	2,7-Dimethylnaphthalene	1.74	0.35
<i>cis</i> -(6)	1.65	2,7-Dimethylnaphthalene	1.74	0.09

<sup>a</sup> Determined in MeCN-TBAP (0.1M) at 250 mV s<sup>-1</sup>.

cases the lowering in peak potential is consistent with the geometrical requirements for  $\pi$  assistance. The fully overlapped para compound is more strained due to *p* orbital compression which is relieved by the formation of a cation-radical. It is apparent that the strain energy term is not the sole cause of the anomalous cathodic shift observed for [2.2]meta compounds.

The formation of a transannular product ( $O_2$  peak) and the effect induced by 5,13-dialkyl substitution suggest the involvement of a transannular cation-radical such as (16). The cation-radical (16) can also be



postulated as an intermediate in reactions with metal salts, such as copper(II) chloride, lead(IV) acetate, and iron(III) chloride all of which are quite effective in promoting transannular dehydrogenation. From competitive experiments the relative rates for dehydrogenation of (9a-c) and (11) were 1 : 160 : 120 : 40 reflecting the importance of (16) especially with R = Me. Solvent effects on metal salt reactions also favour formation of an ion-pair intermediate.<sup>24</sup> The ratio (9d) : (9b) is 1.64.

On nitration with dilute nitric acid in acetic acid (9b) gave (14b) in high yield under very mild reaction conditions.<sup>29</sup> Addition-elimination involving *ipso*-attack of a nitronium ion on a methylated aryl carbon atom has

<sup>27</sup> R. H. Boyd, *Tetrahedron*, 1966, **22**, 119; C.-F. Shieh, D. McNally, and R. H. Boyd, *ibid.*, 1969, **25**, 3653.

<sup>28</sup> T. Sato, *Kagaku no Ryoiki*, 1969, **23**, 672, 765; S. Misumi, *ibid.*, 1974, **28**, 927; Y. Sakata, *ibid.*, p. 947.

<sup>29</sup> N. L. Allinger, M. A. DaRooge, and R. B. Hermann, *J. Amer. Chem. Soc.*, 1961, **83**, 1947; T. Sato, M. Wakabayashi, Y. Okamura, T. Amada, and K. Hata, *Bull. Chem. Soc. Japan*, 1967, **40**, 2363; N. L. Allinger, B. J. Gordon, H.-E. Hu, and R. A. Ford, *J. Org. Chem.*, 1967, **32**, 2272; R. W. Griffin, jun., and R. A. Coburn, *ibid.*, p. 3956.

been postulated but it is highly probable that the reaction involves initial electron transfer to give (16) and nitrogen dioxide. Electrophilic aromatic substitution involving initial electron-transfer has been proposed by Nagakura *et al.*<sup>30</sup> This nitration is accompanied by a transient intense coloration. Preliminary e.s.r. studies showed the development of radical species. It is probable that (16) is involved in other electrophilic reactions of metacyclophanes.

Similar structures can be written for anion-radicals from [2.2]metacyclophanes, *e.g.* (17). The reductive dehydrogenation of (9) and related compounds<sup>9-11,22</sup> can be regarded as proceeding *via* (17) or an equivalent structure.

Compound (9a) and derivatives underwent transannular dehydrogenation under photolytic conditions.<sup>31,32</sup> The reaction occurred in deaerated cyclohexane in the presence of iodine using light of wavelength 253.7 nm with  $\Phi$   $6.2 \times 10^{-3}$ .<sup>31</sup> Moreover, photolytic dehydrogenation was found to occur in the absence of oxidant though in low quantum yield ( $\Phi < 0.01$ ). The reaction is characterized by high quantum yield for a radiationless deactivation process ( $\Phi$  0.99) and the lack of emission.<sup>32</sup> We assume the intermediacy of (16) for oxidant induced reaction. Intramolecular electron-transfer to give a charge-separated intermediate with 8,16-transannular bonding is postulated for photolysis in the absence of oxidant.

#### EXPERIMENTAL

*Materials.*—The compounds used were prepared according to methods described in the literature.

**5,13-Di-*t*-butyl[2.2]metacyclophane (9d).** To tetraphenylethylene-sodium adduct in tetrahydrofuran (200 ml) [from tetraphenylethylene (3.5 g) and sodium (10 g)] was added 3,5-bis(bromomethyl)-*t*-butylbenzene (10 g, 0.031 mol) in tetrahydrofuran (200 ml) over 15 h at  $-50^\circ\text{C}$ . The usual work-up gave (9d) (1.3 g, 26%) as plates from *n*-hexane, m.p. 173–174  $^\circ\text{C}$ ;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>; Me<sub>4</sub>Si) 1.34 (s, Me), 2.08 (ax-CH<sub>2</sub>), 3.08 (eq-CH<sub>2</sub>), 4.10 (t, inner ArH), and 7.07 (d, outer ArH);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>; Me<sub>4</sub>Si) 151.9 (C-5), 138.6 (C-3), 133.8 (C-8), 122.1 (C-4), and 41.3, 34.5, and 31.7 p.p.m. (aliphatic) (Found: C, 89.95; H, 9.95. C<sub>24</sub>H<sub>32</sub> requires C, 90.0; H, 10.0%).

**2,7-Di-*t*-butyl-4,5,9,10-tetrahydropyrene (14c).** (a) *By controlled potential electrolysis.* A solution of (9d) (55 mg,

<sup>30</sup> S. Nagakura and J. Tanaka, *Bull. Chem. Soc. Japan*, 1959, **32**, 734.

<sup>31</sup> S. Hayashi and T. Sato, *Bull. Chem. Soc. Japan*, 1972, **45**, 2360.

0.17 mmol) in acetonitrile (70 ml) containing TBAP (0.1M) was electrolysed at the O<sub>1</sub> potential (1.08 V *versus* s.c.e.) supplied from a potentiostat until efficient electrolysis no longer took place. The electricity consumed was 33.6 C; an e.c.e.c. mechanism required 33.6 C. The pyrene (14c) (100%) was obtained as plates, m.p. 223–224  $^\circ\text{C}$ ; *m/e* 318 (M<sup>+</sup>);  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 1.34 (s, Me), 2.87 (s, CH<sub>2</sub>), and 7.04 (ArH).

(b) *With lead(IV) acetate.* With cooling in an ice-bath, lead(IV) acetate (288.0 mg, 0.40 mmol) in trifluoroacetic acid (10 ml) was added dropwise to a solution of (9a) (100 mg, 0.31 mmol) in dichloromethane (20 ml) over 30 min. The usual work-up gave (14c) in 66% yield.

A similar dehydrogenation occurred when (9d) was treated with copper(II) chloride in acetonitrile<sup>24</sup> and gave (14c) together with a small amount of 2,7-di-*t*-butyl-9,10-dihydropyrene.

*Competitive dehydrogenation between (9b and d).* The above dehydrogenation using lead(IV) acetate was carried out for an equimolar mixture of (9b and d) and the reaction was followed by g.l.c. (SE-30; Chromosorb). The relative rate of dehydrogenation (9d) : (9b) was 1.64.

**2,11-Dithia-6-*t*-butyl-14,16-dimethyl[3.3]metacyclophane.** This was prepared by condensation of 3,5-bis(bromomethyl)-*t*-butylbenzene and 1,3-bis(mercaptomethyl)-4,6-dimethylbenzene in alkaline aqueous ethanol containing benzene giving plates, m.p. 144–145  $^\circ\text{C}$ ;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 1.19 (s, Bu<sup>t</sup>), 2.19 (s, Me), 3.69 and 3.80 (CH<sub>2</sub>), 6.38 and 6.61 (2  $\times$  t, inner ArH), and 6.93 and 7.03 (m, d, outer ArH) (C, 74.0; H, 7.75. C<sub>22</sub>H<sub>28</sub>S<sub>2</sub> requires C, 74.1; H, 7.9%).

**6-*t*-Butyl-12,14-dimethyl[2.2]metacyclophane (12).** This was obtained by pyrolysis of 2,11-dithia-6-*t*-butyl-14,16-dimethyl[3.3]metacyclophane 2,2,11,11-tetraoxide, m.p.  $>290^\circ\text{C}$ , obtained from the above dithia compound on oxidation with 30% H<sub>2</sub>O<sub>2</sub> in AcOH-PhH, using a vacuum pyrolysis furnace similar to that described by Staab.<sup>33</sup> The temperature was maintained at 500  $^\circ\text{C}$  and a pre-heater for sublimation was kept at 300  $^\circ\text{C}$ , yielding plates of (12), m.p. 130–130.5  $^\circ\text{C}$ ;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 1.36 (s, Bu<sup>t</sup>), 2.31 (s, Me), 1.7–2.2 and 2.9–3.5 (2  $\times$  m CH<sub>2</sub>), 4.18 (m, inner ArH), and 7.00 and 7.10 (s, d, outer ArH) (C, 90.35; H, 9.65. C<sub>22</sub>H<sub>28</sub> requires C, 90.35; H, 9.65%).

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<sup>32</sup> K. Sorimachi, T. Morita, and H. Shizuka, *Bull. Chem. Soc. Japan*, 1974, **47**, 987.

<sup>33</sup> H. A. Staab and M. Haenel, *Chem. Ber.*, 1973, **106**, 2190.