Electrochemical Formation of Dianions from Unsaturated Cyclophanes

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A series of [2.$_4$]cyclophanetetraenes and closely related compounds has been shown to undergo reversible two-electron reduction at a mercury electrode in dimethylformamide solution. The cyclophanes which contain a conjugated periphery of 4*n* π-electrons, thus being formally antiaromatic hydrocarbons, form dianions of pronounced stability. A considerable degree of structural and geometrical variation is tolerated.

ELECTROCHEMICAL reduction of unsaturated hydrocarbons in aprotic solvents leads, in general, to the formation of radical anions and dianions. If the electron transfers are reversible, the corresponding half-wave or peak potentials are related to the relative free energies of the species involved. Usually, the difference in the potential for the reduction to the radical anion and the dianion is *ca.* 500 mV in solution.[1] The main factor responsible for this difference, which should be larger in the absence of solvation, is interelectronic repulsion in the HOMO of the dianion.

We recently described the reversible two-electron reduction of [2.$_4$]paracyclophanetetraene (1) at a mercury cathode in dimethylformamide (DMF).[2] A necessary condition for two-electron transfer is that the redox potential for formation of the dianion is more anodic than that for formation of the radical ion (see below), and in such cases, effects that more than compensate the coulombic electron repulsion must be considered. A number of cyclophanes, which are analogues of (1), have been synthesized in this laboratory. In order to test the generality of the electrochemical behaviour shown by (1), and to rationalize it, cyclic voltammetric (c.v.) studies have been made on cyclophanes (2)—(9). The results obtained with the heterocyclophanes (7)—(9) prompted the inclusion of the stilbenes (10)—(12) in the study. Although a complete study, including preparative electrolyses, of (1) has been made by us,[3] the closely related cyclophanes (2)—(9) and the stilbenes (10)—(12) have been investigated solely by electroanalytical methods, namely, cyclic voltammetry and in some cases, direct current polarography.

RESULTS

We have earlier shown [2] that (1) yields a stable dianion in dry DMF at mercury, and the cyclic voltammogram has the characteristics of reversible two-electron behaviour with $E_{pa} - E_{pc} = 30$ mV. The cathodic and anodic peak potentials for (2)—(12), as well as polarographic half-wave potentials and limiting currents for some of them, are listed in Table 1. It is seen that essentially reversible two-electron transfer is obtained also for (2)—(5) and (7)—(9), though the differences $E_{pa} - E_{pc}$ are in some instances larger than 30 mV. Compound (6) behaves quite differently from (1) in our system. No anodic peaks are obtained on the reverse scan. Compounds (10)—(12) give two well separated cathodic peaks, corresponding to the formation of radical anion and dianion, respectively. The first electron transfer is reversible for (10) and (11), and quasi-reversible for (12). The behaviour of *trans*-stilbene, (10) is well known from numerous studies; [4–9] our main reason for including it was to obtain the peak potentials under the same experimental conditions as for the other compounds. The reported half-wave potentials for *trans*-stilbene in DMF differ considerably and are listed in Table 2. It is obvious that values obtained in different laboratories should be compared with caution.

TABLE 1

Polarographic ($E_{1/2}$, i_d) and cyclic voltammetric (E_{pc}, E_{pa}) data for cyclophanes and related compounds. All potentials are given *versus* s.c.e. Substrate concentration 5×10^{-4}M, supporting electrolyte 0.1M-tetraethylammonium perchlorate in DMF

Compound [a]	$E_{1/2}$/V (i_d/μA)	E_{pc}/V	E_{pa}/V
(1)	−1.69 (3.4)	−1.70	−1.67
(2)		−1.53	−1.49
(3)	−1.76 (3.5), −2.32 (10) [b]	−1.77 −2.30, −2.69 [c]	−1.74
(4)	−1.90 (4.0)	−1.91	−1.88
(5)		−1.83	−1.80
(6)		−2.04, −2.36,[d] −2.47,[d] −2.65 [d]	
(7)	−1.72 (3.6)	−1.75	−1.69
(8)	−1.55 (4.0)	−1.56	−1.53
(9)		−1.46	−1.38
(10)		−2.24, −2.58	−2.17
(11)		−2.27, −2.65	−2.20
(12)		−2.18, −2.49	−2.08

[a] For structure, see Figures 1 and 2. [b] Poorly defined wave. [c] Approximate peak heights 1 : 2 : 1. See Figure 1. [d] Poorly resolved peaks. See Figure 2.

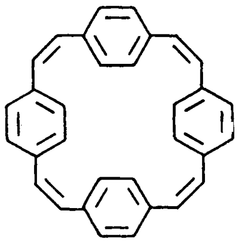
Differently sized mercury drops were used for the cyclic voltammetric experiments on different compounds, so that the peak heights are of limited value in estimating the number of electrons transferred at each peak. Compounds (1), (3), (4), (7), and (8) were also investigated by conventional direct current polarography, which enables one to obtain quantitative current data. The same capillary and mercury pressure (400 mm) was used throughout, and since it is known from previous work [2] that the 3.4 μA wave of (1) represents a 2 e$^-$ process, it is easy to see that (3), (4), (7), and (8) are reduced in 2 e$^-$ processes, too. For compound (6), cyclic voltammetry yielded the number of electrons transferred through comparison with the reduction of (10) at the *same* mercury drop.

DISCUSSION

General Aspects of Consecutive Electron Transfer Steps.—The conversion of a substrate S to its dianion may be formulated thus as in equations (1) and (2). If both electron transfers are sufficiently fast for the particular technique chosen, *e.g.*, stationary electrode cyclic voltammetry, we have reversible charge transfer. The shape of a cyclic voltammogram for two consecutive reversible electron transfer steps will depend on the separation of the redox potentials, $\Delta E^\circ = E^\circ_2 - E^\circ_1$. Some calculated voltammograms for various

$$S + e^- \rightleftharpoons S^{\cdot -};\ E^\circ_1 \tag{1}$$

$$S^{\cdot -} + e^- \rightleftharpoons S^{2-};\ E^\circ_2 \tag{2}$$



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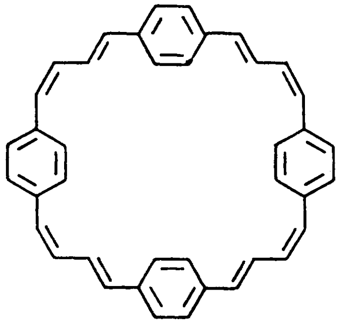

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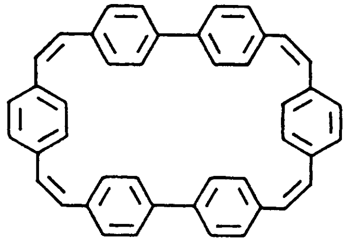

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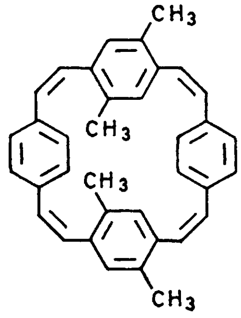

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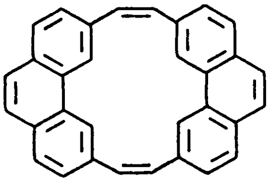

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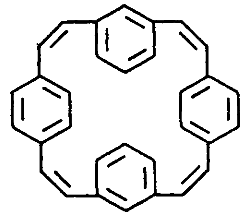

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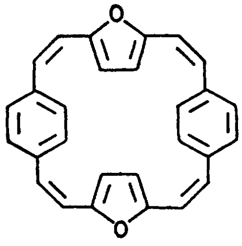

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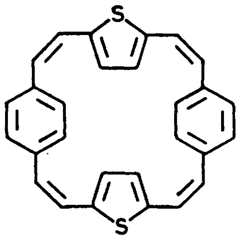

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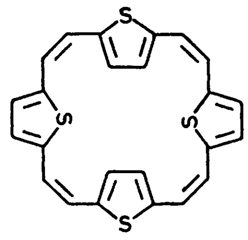

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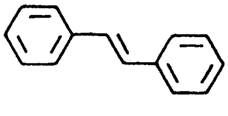

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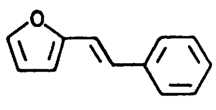

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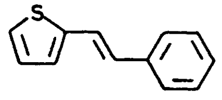

(12)

values of ΔE° are illustrated in a paper by Polcyn and Shain.[11] When $\Delta E^{\circ} \geqslant 180$ mV, the shape of the voltammogram is that of a two-electron process. The peak separation $E_{pa} - E_{pc}$ is then *ca.* 30 mV.[12] A smaller value of ΔE° will lead to a larger peak separation; for example, when $\Delta E^{\circ} = 0$, $E_{pa} - E_{pc} = 42$ mV. Recently, such a case was experimentally demonstrated for a binuclear copper complex.[13,14] When $\Delta E^{\circ} \leqslant -180$ mV, two distinct cathodic peaks and the corresponding anodic peaks are obtained.

Reversible two-electron transfer has been observed by us for (1).[2] Rieke and Copenhafer had earlier demonstrated the same behaviour for 1,3,5,7-tetraphenylcyclo-octatetraene,[15] with a half-wave potential for the reduction of −1.72 V. They used a different solvent, butyronitrile, but the same electrode, mercury, and supporting salt, tetraethylammonium perchlorate, as in our study.

TABLE 2

Reported polarographic half-wave potentials *versus* s.c.e. for the reduction of *trans*-stilbene in DMF at a mercury cathode

Supporting salt [a]	$E_{1/2}^{1}$/V	$E_{1/2}^{2}$/V	Ref.
TBAI, 0.175M	−2.21	−2.58	4
TBAI, 0.2M	−2.141 ±0.013	−2.498 ±0.022	5
TBAI, 0.1M	−2.15	not rep.	6
TEAP, 0.1M	−2.21 [b]	−2.55 [b]	
TEAP, 0.1M	−2.36	−2.76	7
TEAI, 0.1M	−2.19	−2.57	8
TMAT, saturated	−2.17	−2.60	9

[a] TBAI = Tetrabutylammonium iodide, TEAP = tetraethylammonium perchlorate, TEAI = tetraethylammonium iodide, TMAT = tetramethylammonium tetrafluoroborate. [b] Calculated from c.v. peak potentials obtained in this work (Table 1). $E_{1/2} = E_{pc} + 0.03$V.[10]

Factors causing Two-electron Behaviour.—The cathodic reduction of cyclo-octatetraene (COT) and some of its phenyl derivatives has been discussed by Rieke and Copenhafer.[15] The electrolyte effect on the reduction of COT has been discussed in two recent papers.[16,17] Rieke and Copenhafer rationalize the reversible two-electron behaviour of 1,3,5,7-tetraphenylcyclo-octatetraene as an anodic shift of the second electron transfer, which will cause it to merge with the first one.

Hückel-aromatic hydrocarbons show a potential separation of *ca.* 0.5 V for formation of the radical anion and the dianion in solution.[1] The same difference for *trans*-stilbene is *ca.* 0.35 V (Table 2). In anti-Hückel hydrocarbons, the separation between the first and the second electron transfer varies depending on the particular compound and the conditions. The cathodic reduction of COT in dimethyl sulphoxide [16] or DMF [17] is influenced by the cation of the supporting salt. With tetramethylammonium iodide in DMF, the potential difference is 0.2 V.

Larger anti-Hückel rings have also been studied. For [12]annulene, two reversible waves were found in tetrahydrofuran at −80 °C with $E_{1/2}$ *versus* a Hg pool of −1.35 and −2.00 V.[18] The next member, [16]annulene, in DMF at 0 °C gave $E_{1/2}$ *versus* a 0.1M-KCl calomel electrode of −1.23 and −1.52 V for the first and second electron transfer, respectively.[19]

In a formal sense, (1) may be regarded as an anti-Hückel compound since its periphery contains 24 π-electrons. The clear-cut two-electron behaviour of (1) in DMF [2] means that after formation of the radical anion, the introduction of the second electron is energetically more favoured than in the case with common aromatic hydrocarbons.

The dianion of (1) is ostensibly non-basic.[2,3] In c.v. experiments in normally dried DMF it was possible to hold the potential for several seconds at a value where the dianion is present, and then to reoxidize the latter with an i_{ox}/i_{red} ratio of unity.

Since the dianion of (1) is apparently a moderately weak base, we attempted to prepare it through proton abstraction from dihydro-(1) with butyl-lithium and *NNN′N′*-tetramethylethylenediamine.[20] No deuterium was incorporated into dihydro-(1) on addition of D_2O.

The c.v. and polarographic studies in this work have employed DMF as the solvent. In the less polar 1,2-dimethoxyethane, the radical anions of (1) and (7)—(9) have been prepared with potassium metal. Their e.s.r. and ENDOR spectra have been studied.[21] Slow rotation of the benzene rings in ($1^{\cdot -}$) and ($7^{\cdot -}$) was observed. In the latter only ion-pairing seemed important in pure 1,2-dimethoxyethane but decreased on addition of hexamethylphosphoramide.

There is no contradiction between the above work and our electrochemical studies. In DMF, the dianions are sufficiently better solvated than in 1,2-dimethoxyethane to allow two-electron reduction of the cyclophanes.

Reduction of the Isocyclic Compounds.—We have found that [4_4]paracyclophaneoctaene (2) which formally has a perimeter with 32 π-electrons, behaves similarly to (1) on cathodic reduction. The peak potential is 170 mV more anodic than that of (1), and the peak separation $E_{pa} - E_{pc}$ is 40 mV, corresponding to ΔE_0 *ca.* 0.[11] The n.m.r. and u.v. spectra show that (2) is more planar than (1), which is also a reasonable conclusion from inspection of molecular models (CPK) of the two compounds.

The same number of π-electrons, 32, along the perimeter is contained in the biphenylophane (3). However, 24 of these are part of benzene rings. Moreover, (3) cannot be very planar. It is interesting to find, however, that (3) behaves almost as (1) on reduction. The peak separation is the same as in (1), but the peaks are shifted 70 mV more cathodic. New, irreversible peaks appear (Figure 1) at more cathodic potentials. They presumably involve reduction of the biphenyl units and have not been further investigated. Addition of phenol caused all peaks to become irreversible.

The demand for planarity of the π-system has been further investigated. The introduction of substituents in the benzene rings, for example four methyl groups as in (4), causes a steric distortion of the π-system towards a less planar structure. Cyclophane (4) exists as two conformational isomers which rapidly interconvert on the n.m.r. time scale at room temperature. The inductive effect of the four methyl groups in the reduction potential does not suffice to account for the cathodic shift of 210 mV with respect to (1).

Another example of a distorted π-system is offered by the phenanthrenophane (5). N.m.r. and u.v. spectra show that there is only minor conjugation between the two phenanthrene units. A molecular mechanics calculation has given an equilibrium angle between the planes of the phenanthrenes of 67°.[22] The calculated energy barrier for inversion is $\leqslant 88$ kJ mol^{-1}, which comes from distortion of the bond angles at the double bonds and from interactions between the inner hydrogens. The phenanthrenophane (5) shows the same behaviour as (1) on reduction. A dianion is reversibly formed at 130 mV more negative potential than (1), with a peak separation of 30 mV. Phenanthrene itself is reduced at a much more negative potential, -2.44 V.[8]

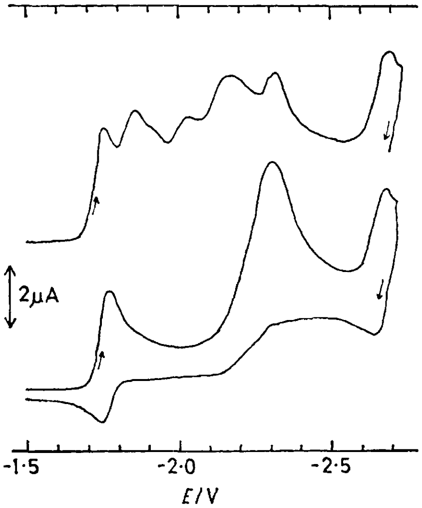

FIGURE 1 Cyclic voltammogram of (3) in DMF–0.1M-TEAP. [Substrate] 5×10^{-4}M. [Phenol], lower trace 0; upper trace 2×10^{-3}M. Sweep rate 40 mV s^{-1}. Potentials *versus* s.c.e.

Compound (6), which has two *meta*-substituted benzene rings, behaves very differently from the other compounds. No structure with a fully conjugated periphery can be drawn. Its cyclic voltammogram (Figure 2) shows no anodic peaks, suggesting fast protonation by residual water in the solvent. The species formed on initial electron transfer is probably a dianion which is rapidly protonated and further reduced. By comparison of the peak height with that of a known 1 e$^-$ process, reduction of (10), at the same mercury drop and with the same sweep rate, it could be concluded that the first peak in the reduction of (6) corresponds to four electrons. Addition of phenol to the solution gave an anodic shift of the first peak but did not increase its height (Figure 2), and a second peak, also corresponding to four electrons, was obtained at E_{pc} -2.25 V, very close to the potential of reduction of (10), -2.24 V. A coulometric electrolysis of (6) in phenol-containing DMF, followed by product analysis by ^{1}H n.m.r. revealed that at the potential corresponding to the first peak, 4 F mol^{-1} were consumed. The complexity of the n.m.r. spectrum suggested that at least two compounds were present, and attempts at separation were unsuccessful.

Reduction of the Heteroaromatic Compounds.—The [2.$_4$]cyclophanetetraene (7) with two furan rings gives a value of E_{pc} which is 50 mV more negative than that of (1). It is understandable that a compound with electron-rich furan rings is more difficult to reduce than the benzene analogue. The separation between E_{pc} and E_{pa} amounts to 60 mV. Since the polarographic waveheight shows that a two-electron reduction is at hand, the peak separation does not imply a reversible one-electron process.

Compound (8) with two thiophen rings is easier to reduce than (1) and the peak separation is 30 mV (Table 1). Compound (9) with four thiophen rings is even easier to reduce, but the peak separation is 80 mV. Since carbon atoms α to sulphur can sustain the negative charge in the dianions because of overlap with empty *d* orbitals on sulphur, the progressively anodic shift in the series (1), (8), (9) can be easily rationalized. The peak separations of (7) and (9) need explanation. One reason could be that the condition $\Delta E_0 \geqslant 180$ mV necessary for two-electron reversible behaviour[11] is not fulfilled. Another reason could be that the *rate* of electron transfer is slower in (7) and (9) than in (1) and (8). In the latter case, c.v. at different sweep rates should produce different values of the peak separations.

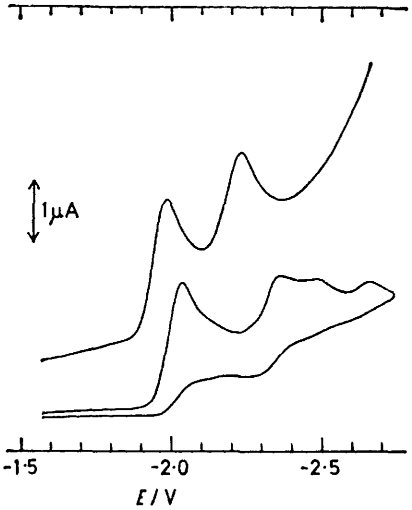

FIGURE 2 Cyclic voltammogram of (6) in DMF–0.1M-TEAP. [Substrate] 5×10^{-4}M. [Phenol], lower trace 0; upper trace 2×10^{-2}M. Sweep rate 25 mV s^{-1}. Potentials *versus* s.c.e.

Within the admittedly narrow range 25—100 mV s^{-1}, the peak separations were constant, however.

To allow a distinction between the two above possibilities, (10)—(12) were included in the study. In these compounds, the first electron transfer is well separated from the second one, and $E_{pa} - E_{pc}$ for the first electron transfer should have the value 60 mV if reversibility is at hand, *i.e.*, at sufficiently low sweep rate. Table 1 shows that reversibility is observed for

(10) and (11), but not for (12), where the peak separation is 100 mV. This would suggest a kinetic effect on the electron transfer, but preliminary experiments with phase-sensitive alternate current polarography have not verified this.[23]

The Choice of Reference Electrode.—During the early stages of this work, we experienced difficulties in reproducing our potential measurements to better than 30—50 mV if measurements were made on different occasions and/or by different workers. The commercial s.c.e. first used was galvanically connected to the DMF *via* an aqueous solution of tetraethylammonium bromide (0.1M), and a plug of methylcellulose gel made with 0.1M-tetraethylammonium perchlorate (TEAP) in DMF.[24] No doubt uncontrollable liquid junction potentials enter, and a survey of the literature concerning the reduction of *trans*-stilbene (10) in DMF (Table 2) demonstrates the poor agreement between different laboratories. We therefore switched to the use of the system Ag–0.01M-$AgNO_3$–0.1M-TEAP in DMF described in the literature.[25] A methylcellulose plug serves as the separator. This arrangement gave reproducible potentials within 10 mV. Potentials *versus* this electrode are 0.43 V more cathodic than *versus* s.c.e. Throughout this paper, potential values are *versus* s.c.e. but are calculated.

The literature contains more than one statement [26,27] questioning the stability of this electrode; silver(I) ion is said to be reduced by the DMF. This is hard to understand, since the potential of our Ag–0.01M-$AgNO_3$ electrode *versus* s.c.e. is 0.43 V, while the oxidation of DMF at a noble metal anode takes place at 1.6 V *versus* s.c.e.[28] We noted, however, that an initial discolouration to a yellow tint takes place upon dissolving silver nitrate in DMF, and we think that this is due to colloidal silver produced by reduction of silver ion by the residual formic acid in the solvent.

EXPERIMENTAL

Compounds.—The syntheses of the following cyclophanes have been described: [2.$_4$]paracyclophanetetraene (1),[29] [4.$_4$]paracyclophaneoctaene (2),[30] [2.2.0.2.2.0]paracyclophanetetraene (3),[31] [2.2](3,6)phenanthrenophanediene (5),[32] all-*cis*-[2.$_4$]metaparametaparacyclophanetetraene (6),[33] [2](2,5)furano[2]paracyclo[2](2,5)furano[2]paracyclophanetetraene (7),[31] [2](2,5)thiopheno[2]paracyclo[2]-(2,5)thiopheno[2]paracyclophanetetraene (8),[31] and [2.$_4$]-(2,5)thiophenophanetetraene, (9).[34] The tetramethyl[2.$_4$]-paracyclophanetetraene (4) was prepared from 2,5-dimethylbenzene-1,4-dicarbaldehyde and the bistriphenylphosphonium salt from 1,4-bis(bromomethyl)benzene by the same method as for the other cyclophanes,[31] m.p. 228—232 °C, δ (270 MHz; $CDCl_3$; 60 °C) 6.97 (4 H, s, ArH) and 6.96 (8 H, s, ArH), 6.57 (4 H, d, olefinic H) and 6.47 (4 H, d, *J* 12.2 Hz, olefinic H), and 2.07 (12 H, s, CH_3). The n.m.r. spectrum was temperature dependent, consistent with a slow rotation of the dimethyl-substituted benzene rings.[35]

trans-Stilbene (10), was a commercial sample (scintillation grade). 2-(2-Styryl)furan (11) and 2-(2-styryl)thiophen (12) were prepared from the corresponding aldehydes and diethyl benzylphosphonate.[36]

Polarography and Cyclic Voltammetry.—The same electrolyte, electrodes, and equipment was used as in previous work,[37] except that the Ag–$AgNO_3$ reference electrode described by Butler [25] was used.

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