

## Short Communication

Electrochemical Reduction of  
[2<sub>4</sub>]Paracyclophanetetraene.  
A Reversible Two-electron ProcessKJELL ANKNER, BO LAMM,\*  
BENGT THULIN and OLOF WENNERSTRÖMDepartment of Organic Chemistry, Chalmers  
University of Technology and University of  
Göteborg, P.O.B., S-402 20 Göteborg, Sweden

The large ring compound [2<sub>4</sub>]paracyclophanetetraene, **1**, has recently been synthesized in our laboratory.<sup>1</sup> Since it contains a conjugated perimeter of 24  $\pi$  electrons, it can formally be regarded as a derivative of [24]annulene, although it does not show a large paramagnetic ring current.<sup>2</sup>

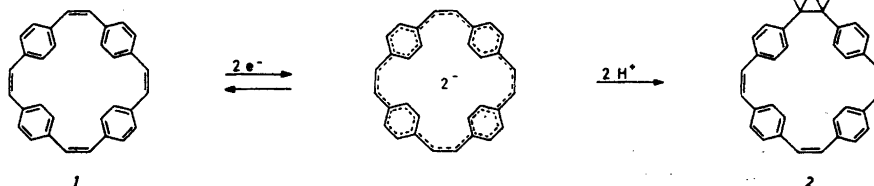
Electrochemical reductions of smaller  $4n$   $\pi$ -electron systems have been carried out by other workers. A recent, careful study of cyclooctatetraene<sup>3</sup> has shown that consecutive one-electron transfers lead to the radical anion and the dianion.

The stepwise reduction of [12]annulene<sup>4</sup> and of [16]annulene<sup>5</sup> to the corresponding dianions is also known. In either case, two separate one-electron transfers are observed.

We now report a simple and completely reversible two-electron reduction of [2<sub>4</sub>]paracyclophanetetraene, **1**, to its dianion which can be quenched by acetic acid to give [2<sub>4</sub>]paracyclophanetriene, **2** (Scheme 1).

A cyclic voltammogram of **1**, obtained at a hanging mercury drop electrode in DMF containing tetraethylammonium perchlorate (TEAP), is shown in Fig. 1. The separation between the cathodic and the anodic potentials is 30 mV, which is essentially the theoretical value for a reversible two-electron transfer.<sup>6</sup>

\* To whom correspondence should be directed.



Scheme 1.

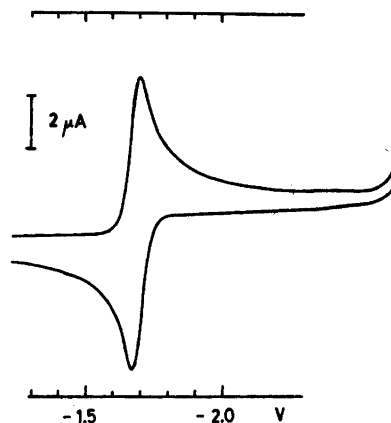


Fig. 1. Cyclic voltammogram of [2<sub>4</sub>]paracyclophanetetraene. Hanging Hg drop, DMF solvent, 0.1 M tetraethylammonium perchlorate. Pot. vs. SCE. Scan rate 0.1 V s<sup>-1</sup>.

The cathodic peak potential was -1.70 V vs. SCE. The scan rate was 0.1 V s<sup>-1</sup>. The anodic peak successively decreased in the presence of increasing amounts of phenol and disappeared when the sixfold molar amount of phenol had been added. A conventional DC polarogram was also recorded giving  $E_{1/2} = -1.69$  V vs. SCE. A plot of  $\log i/(i_d - i)$  vs.  $E - E_{1/2}$  had a slope of -0.030, indicating a reversible two-electron process.<sup>7</sup>

A situation superficially similar to that shown in Fig. 1 has been observed for the reduction of tetraphenylethylene to its dianion.<sup>8</sup> A platinum electrode was used, and the solvent/supporting electrolyte system was tetrahydrofuran containing tetrabutylammonium perchlorate. Cyclic voltammograms were recorded at scan rates between 0.06 and 0.6 V s<sup>-1</sup>. The separation of

the cathodic and the anodic peak potentials, extrapolated to zero current, was found to be 60 mV. It was independently shown that a two-electron process was at hand.<sup>8</sup> The peak separation ruled out a Nernstian simple two-electron transfer. Two successive, reversible electron transfers at potentials separated by less than 100 mV were postulated.

One factor which could determine the potential separation between two consecutive one-electron transfer steps in the reduction of aromatic hydrocarbons is the coulombic repulsion between the two entering electrons.<sup>9a</sup> Other factors such as conformational changes, ion-pairing, and solvent reorganization should also be considered.<sup>9a</sup> Conformational changes occur during the reduction of cyclooctatetraene<sup>10</sup> and tetraphenylethylene.<sup>9b</sup> However, the cyclophane *1* is rather planar<sup>11,12</sup> and not expected to become more planar on reduction because the steric interaction between the internal hydrogen atoms should prevent this. Ion-pairing is usually not important in polar solvents but could well be an important factor in ethereal solvents. The data obtained in this work for the reduction of cyclophane *1* demonstrate that the electronic repulsion in the dianion is unimportant, at least in a polar solvent such as DMF, probably due to the size of the molecule.

A preparative electrolysis of [2<sub>4</sub>]paracyclophanetetræne, *1*, was performed in the same medium and supporting electrolyte and with the same reference electrode as in the analytical experiment (DMF, 0.1 M TEAP). A cell divided by a glass frit and with a mercury cathode surface of 12 cm<sup>2</sup> was used. To the catholyte (50 ml) was added glacial acetic acid (0.3 ml) and the mixture was pre-electrolysed at -1.80 V. After addition of [2<sub>4</sub>]paracyclophanetetræne, *1* (200 mg), the electrolysis was performed at -1.70 V. The current was allowed to decrease to its background level. The charge consumption was 1.93 F mol<sup>-1</sup>. Water (100 ml) was added to the catholyte, and the mixture extracted with diethyl ether several times. The ether fractions were washed with water, dried over sodium sulfate and the solvent evaporated. Recrystallisation of the residue from ethanol gave [2<sub>4</sub>]paracyclophanetriene, *2* (124 mg, 62%, m.p. 168–170°C). IR (KBr): 3015 (m), 2935 (m), 2860 (m), 1605 (m), 1510 (s), 1425 (s), 1268 (m), 1187 (m), 1105 (s), 895 (s), 835 (s), and 745 (m) cm<sup>-1</sup>. UV (ethanol): λ<sub>max</sub> 283 nm (ε 25 000) and 225 nm (36 500). <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>): δ 7.18 (4 H, d), 7.12 (4 H, d, *J* 8.5 Hz), 7.09 (4 H, d), and 6.79 (4 H, d, *J* 8.5 Hz), aromatic protons, 6.52 (6 H, broad s), olefinic protons, and 2.88 (4 H, s), benzylic protons. MS (65 eV): *m/e* 410 (100%, m<sup>+</sup>), 205 (34, M<sup>2+</sup>), 204 (6), 203 (6), 202 (9), 193 (7), 191 (7), 115 (9), and 91 (8). Abs. mass 410.2036 ± 0.003; calc. for C<sub>32</sub>H<sub>26</sub> 410.2035.

*Acknowledgement.* Financial support from the Swedish Natural Science Research Council is gratefully acknowledged.

1. Thulin, B., Wennerström, O. and Högberg, H.-E. *Acta Chem. Scand. B* 29 (1975) 138.
2. Strand, A., Thulin, B. and Wennerström, O. *Acta Chem. Scand. B* 31 (1977) 521.
3. Jensen, B. S., Ronlán, A. and Parker, V. D. *Acta Chem. Scand. B* 29 (1975) 394.
4. Oth, J. F. M. and Schröder, G. *J. Chem. Soc. B* (1971) 904.
5. Oth, J. F. M., Anthoine, G. and Gilles, J.-M. *Tetrahedron Lett.* (1968) 6265.
6. Cauquis, G. and Parker, V. D. In Baizer, M. M., Ed., *Organic Electrochemistry*, Dekker, New York 1973, p. 118.
7. Fry, A. J. *Synthetic Organic Electrochemistry*, Harper & Row, New York 1972, p. 36.
8. Funt, B. L. and Gray, D. G. *J. Electrochem. Soc.* 117 (1970) 1020.
9. Szwarc, M. and Jagur-Grodzinski, J. In Szwarc, M., Ed., *Ions and Ion Pairs in Organic Reactions*, Wiley, New York 1974, Vol. 2; a. p. 91; b. p. 99.
10. Katz, T. J. and Strauss, H. L. *J. Chem. Phys.* 32 (1960) 1873.
11. Ljungström, E., Lindquist, O. and Wennerström, O. *Acta Crystallogr. B. In press.*
12. Liljefors, T. and Wennerström, O. *Tetrahedron* 33 (1977) 2999.

Received September 22, 1977.