

ELECTROCHEMICAL BEHAVIOR OF LAYERED ANNULENES

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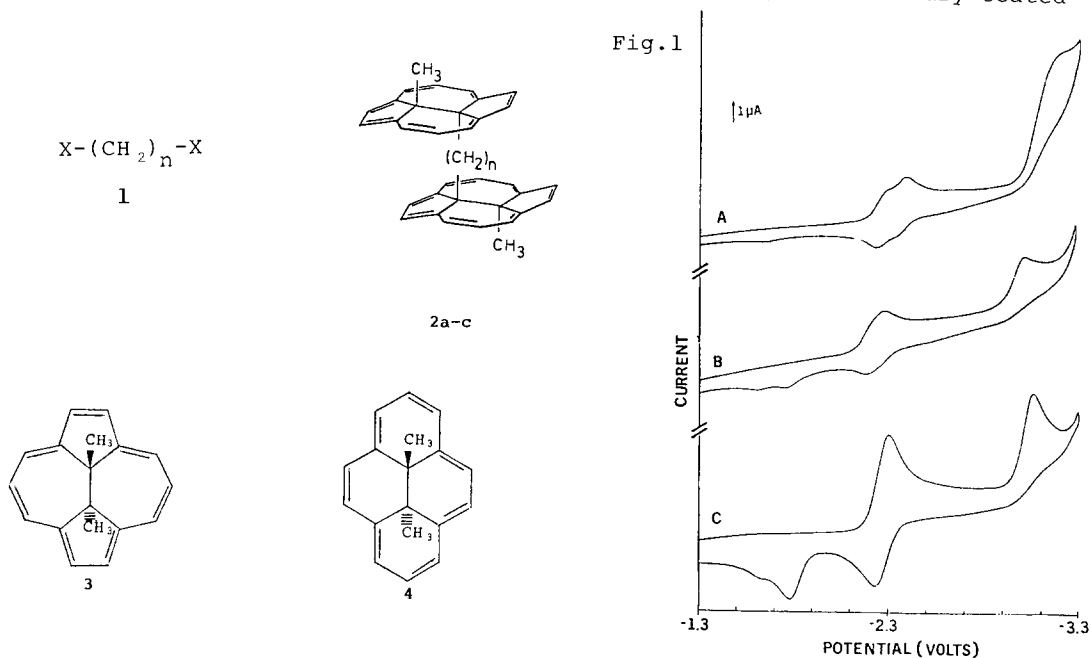
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**Summary:** The cyclic voltammetric behavior of a series of dimeric [14] annulenes was examined and compared with the monomer. The data suggest a significant degree of interaction between the annulene rings when a three-carbon chain connects them, little or no interaction with an eight-carbon chain, and weak interaction with a four-carbon chain.

A large number of studies have addressed the question of the electrochemical behavior of substances containing two identical, but isolated redox systems (1). Such studies are capable of measuring the degree of interaction between the two redox systems upon addition or removal of one or more electrons.<sup>1</sup> A variety of such systems, including bridged biferrocenes,<sup>1b</sup> polymeric substances,<sup>1c</sup> nitroarenes,<sup>1d</sup> and inorganic complex ions,<sup>1e</sup> has been examined. However, no such study has explored the degree of electronic interaction between two non-benzenoid aromatic systems linked as in 1, with the exception of bicyclooctatetraenyl<sup>2</sup> and certain diazulenyls.<sup>3</sup> These represent special cases, both because the pi-systems are directly bound (n=0) and because in the latter substances the electron distribution in the individual components is quite unsymmetrical. A recent report described an ESR spectroscopic study of radical anions derived from the layered annulenes 2a-c.<sup>4</sup> The results demonstrated substantial electron-delocalization between the two pi-systems in 2a,<sup>-</sup> no interaction in 2c,<sup>-</sup> and marginal overlap in 2b,<sup>-</sup> the ESR spectrum of which is best interpreted in terms of the presence of 70% of a spin-delocalized radical anion and 30% of a spin-localized ion. We now report the results of an investigation into the electrochemical behavior of 2a-c, which provides further information bearing on the degree of interaction

between the annulene rings in reduced forms of these substances.

Compounds **2a-c** were examined by cyclic voltammetry at a mercury-coated



platinum electrode<sup>5</sup> in dimethylformamide (DMF) containing 0.1M tetrabutylammonium perchlorate (TBAP), at a scan rate of  $100 \text{ mV sec.}^{-1}$ . The monomeric annulene **3** was also examined under the same conditions, for comparison with both **2a-c** and the previously-studied<sup>6</sup> isomeric annulene **4**.

The cyclic voltammogram of **2a** is shown in Fig. 1A. It consists of two closely spaced reversible waves near -2.3V, an irreversible wave at -3.2V whose height corresponds to a total uptake of four electrons, and a very small anodic wave at ca. -1.7V. The two waves near -2.3V are associated with stepwise one-electron reduction of the individual annulene units of **2a** to the corresponding radical anions. Because the individual reduction potentials cannot be measured directly from the voltammogram, the values in Table I were obtained by comparison of the experimental trace with a series of computer-simulated voltammograms,<sup>7</sup> with the best match corresponding to  $E_1^0 = -2.26 \text{ V}$  and  $E_2^0 = -2.36 \text{ V}$  (Table I).

The cyclic voltammograms of **2b** and **2c** exhibit distinctive differences from that of **2a** and from each other. For **2b** (Fig. 1B), the two waves near -2.2V are barely perceptibly resolved, the wave at -3.0V corresponds to uptake of two electrons, and the two anodic waves between -1.6 and -1.8V are larger than the corresponding wave in **2a**. Computer simulation shows that for Fig. 1B,  $E_1^0 = -2.21 \text{ V}$  and  $E_2^0 = -2.29 \text{ V}$ . In the voltammogram of **2c** (Fig. 1C), the two redox couples at -2.3V are completely coalesced, the wave near -3.1V is a two-electron wave, and the anodic waves between -1.6 and -1.8V are considerably larger than with either

Table I. Reduction Potentials of [14] Annulenes

Compound	n	$-E_1^0(V)$	$-E_2^0(V)$	$\Delta E^0(V)$	Interaction Energy (kcal/mole) <sup>a</sup>
2a	3	2.26	2.36	.100	1.5
2b	4	2.21	2.29	.080	1.0
2c	8	2.239	2.283	.044	0-0.2
1	$\infty$	2.242	2.278	.036	0
3			2.26 <sup>b</sup>		
4			2.26 <sup>c</sup>		

<sup>a</sup>( $\Delta E - 0.036V$ ) x 23.06 kcal/volt. <sup>b</sup>Second reduction step occurs at  $-3.00V$ .

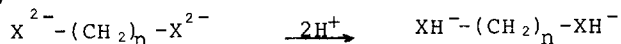
<sup>c</sup>Second reduction step occurs at  $-3.05V$ . <sup>d</sup>Apparent peak height variations in Fig. 1 are due to variations in substrate concentration, due in turn to the small amounts of available material.

2a or 2b. The cyclic voltammogram of 3 (not shown) is identical to that of 2c, except that the cathodic and anodic peak potentials near  $-2.3V$  are closer together (65mV with 3, and 75 mV with 2c). This difference could represent a very weak electronic interaction between the two rings in 2c (*vide infra*), but might simply be due to experimental error.

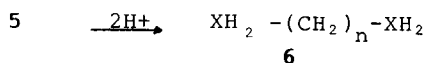
These data are best understood in terms of the theoretical voltammogram for a substance with two identical redox groups separated by a chain of infinite length. Such a voltammogram can be generated by computer simulation for two redox processes with  $E^0 \rightarrow E^0_{\text{monomer}} \pm 0.018V$  at  $25^\circ C$ , where the latter term arises from simple statistical considerations.<sup>1c,d</sup> In practice, many substances of structure 1 exhibit such limiting behavior when  $n \geq 3$ .<sup>1a</sup> The voltammograms of 2a and 2b, however, exhibit clear evidence of electronic interaction between the two pi-systems (Table I). That of 2a corresponds to two reduction steps separated by 100 mV; subtracting the statistical contribution of 36mV leaves a residual spacing of 64mV, or 1.5 kcal/mole ( $1V=23.06$  kcal/mole). This interaction energy is in principle a composite of two terms, arising from both stabilization of  $2a^{\cdot-}$  by electron-delocalization over both rings, and destabilization of  $2a^{2-}$  because of electron-repulsion between the two negatively-charged rings. The data do not permit dissection of the 1.5 kcal/mole value into these two terms, but the ESR spectrum of  $2a^{\cdot-}$  affords clear evidence for electron-delocalization<sup>4</sup> and therefore suggests that the first effect is more important. By a similar analysis the interaction energy in 2b is found to be ca. 1.0 kcal/mole and again the ESR spectrum<sup>4</sup> of  $2b^{\cdot-}$  is consistent with weak, but measurable stabilization of the radical anion by inter-ring electronic delocalization. Thus the annulene rings in 2a,b are seen to interact surprisingly strongly, perhaps because of the unique geometry in these substances, in which the chain of methylene groups

holds the two rings in close face-to-face proximity.

The phenomena taking place in the voltammograms of **2a-c** and **3** in the vicinity of -3.2V and -1.7V also deserve attention. By analogy to the electrochemical behavior of many unsaturated hydrocarbons,<sup>8</sup> these waves correspond to reduction of **3** to a dianion and reduction of **2a-c** to tetraanions. The wave heights at -2.3 and -3.2V should therefore be equal. They are, for **2b,c** and **3**. Furthermore, the irreversible nature of the reduction shows that both rings of the tetraanion undergo rapid chemical reaction, presumably by proton abstraction from the medium, i.e.,



The anodic wave (or waves) in the vicinity of ca. -1.6 to -1.8V, again, by good literature<sup>8</sup> precedent, are associated with oxidation of **5** to a reactive neutral radical. The four electron wave-height at -2.2V for **2a** and the almost total absence of an anodic wave at -1.7V for this substance provide evidence for strong inter-ring destabilizing electron-repulsion in the species **5** derived from **2a**; apparently this dianion undergoes further chemical reaction (because of the two negative charges in close proximity), leading to further electron-uptake. Probably this involves uptake of two further protons by **5** to afford a tetrahydro derivative (**6**), which then undergoes two electron reduction at the very negative



potential at which it is formed.

Finally, the remarkable similarity between the reduction potentials of **3** and the isomeric dihydropyrene (**4**) should be noted (Table I). This fact gives us confidence that in these systems we are observing electrochemical behavior characteristic of 14-electron (Hückel  $4n + 2$ ) annulene systems.<sup>9</sup>

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