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THE SYNTHESIS OF 2,3,6,7-DIBENZOBICYCLO[6.2.0]DECA-2,6,8-TRIEN-4-YNE-9,10-DIONE AND 2,3,6,7-DIBENZOBICYCLO[6.2.0]DECA-2,4,6,8-TETRAENE-9,10-DIONE. THE ELECTROCHEMISTRY OF CYCLOBUTENEDIONES ("CYCLOBUTADIENOQUINONES").[1]

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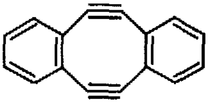
Syntheses of sym-dibenzo-1,5-cyclooctadiene-3,7-diyne (1) and sym-dibenzo-1,3,5-cyclooctatrien-7-yne (2), in which the conjugated eight-membered rings appear to be planar,[2] have recently been described.[3] It was of interest to prepare and study the electrochemistry of the related 2,3,6,7-dibenzobicyclo[6.2.0]deca-2,6,8-trien-4-yne-9,10-dione (3), in which cyclobutenedione ("cyclobutadienoquinone")[4] is fused to a planar conjugated eight-membered ring. We now describe the realization of this objective, as well as the synthesis of 2,3,6,7-dibenzobicyclo[6.2.0]deca-2,4,6,8-tetraene-9,10-dione (4), in which cyclobutenedione is fused to a nonplanar conjugated eight-membered ring.



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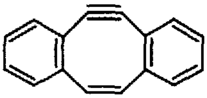

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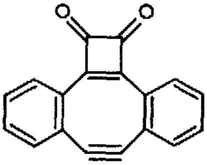

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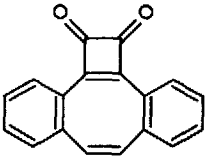

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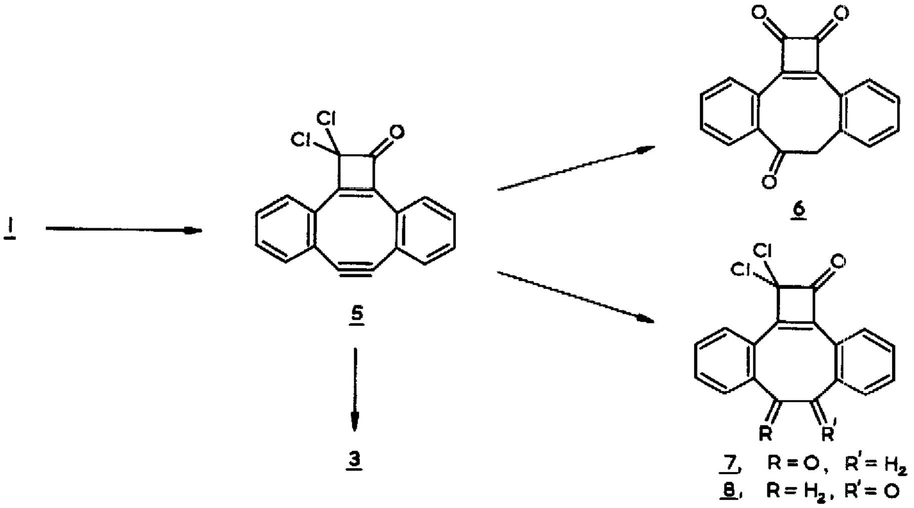
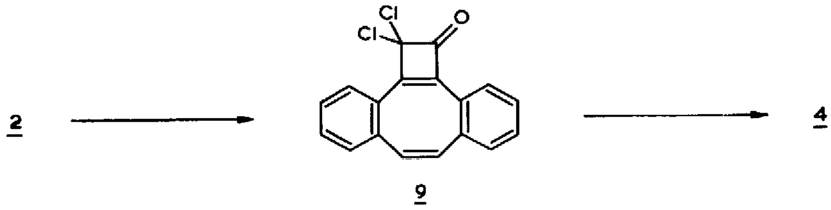
It is known that the [2+2]cycloaddition of dichloroketene to nonactivated acetylenes proceeds well only when the triple bond is strained.[5] The acetylenes in 1 are strained,[2] and reaction of this substance with an excess of dichloroketene (generated in situ from dichloroacetyl chloride and triethylamine)[6] in pentane at 20° for 12 hr gave 42% of the monoadduct 5[7] as red needles, mp 144-145° dec.[8] Attempted hydrolysis of the dichloroketone 5 to the cyclobutenedione 3 with conc. H_2SO_4[4] at 65° for 2 hr resulted also in hydration of the strained acetylene, and gave the trione 6 as pale yellow crystals, mp 173-174°[8] in 70% yield. Unfortunately, hydration of the acetylene appears to occur prior to hydrolysis of the gem-dichloride, since treatment of 5 with conc. H_2SO_4 under milder conditions (20° for 10 sec) led to a mixture of the hydrated products 7 and 8[7] as yellow crystals, mp 123-125°.



After some experimentation, it was found that the desired conversion of 5 to 3 could be effected by means of excess silver trifluoroacetate (1 hr in boiling benzene), a reagent which has been used previously for the hydrolysis of *gem*-dibromides to ketones.^{9} Filtration, shaking of the filtrate [presumably containing the *gem*-bis(trifluoroacetate)] with water, and evaporation, gave the very unstable cyclobutenedione 3 in good yield^{10} as orange-red crystals, which rapidly decomposed on standing or on attempted melting point determination; m/e 256.054 (calcd. 256.052); ^{1}H nmr (CDCl$_3$, 100 MHz, CAT) τ 1.45-3.45 (complex m); ir (KBr) ν_{max} 1770 (s), 1750 (s) cm^{-1} (cyclobutenedione). The electronic spectra of 5 [λ_{max} (hexane) 250 (ε 32,500), 275 (80,000), 283 (97,300), 310 (2750), 326 (2200), 362 (7000), 382 nm (7800)] and 3 [λ_{max} (EtOH) 272 (ε 23,800), 282 (31,700), 363 (2700), 382 nm (2700)^{11}] resemble those of 1 and 2,^{3} with the expected bathochromic shift, and the eight-membered rings in these compounds are presumably also planar.

The monoacetylene 2 was converted to the cyclobutenedione 4 in an analogous manner. Thus, reaction of 2 with dichloroketene, as before, gave the dichloroketone 9^{7} as yellow crystals, mp 158-160°,^{8} in 17% yield. Treatment of 9 with silver trifluoroacetate (5 hr in boiling benzene),



followed by shaking with water, then yielded 23% of the stable dione 4^{7} as pale yellow crystals, mp 198-199°; m/e 258.068 (calcd. 258.068); ^{1}H nmr (CDCl$_3$, 100 MHz, CAT) τ 2.40-2.85 (including a sharp band at τ 2.76) (m, 8H, benzenoid), 3.53 (s, 2H, olefinic); ir (KBr) ν_{max} 1780 (s), 1765sh (s) cm^{-1} (cyclobutenedione). The electronic spectra of 9 [λ_{max} (cyclohexane) $\sim$230sh (ε 23,600), 259 (33,900), 310 nm (6600)] and 4 [λ_{max} (EtOH) 265 (ε 13,600), $\sim$315sh nm (2700)] bear little resemblance to those of the corresponding acetylenic analogs 5 and 3, and the eight-membered rings in these compounds are presumably nonplanar. This is confirmed by the ^{1}H nmr spectra of 9 and 4, in which the olefinic proton resonances (9: τ 3.45; 4: τ 3.53)[12] give no indication of any appreciable paramagnetic ring current in the [8]annulene rings.

The electrochemical reduction of 3 first to the radical anion and then to the dianion 10 was examined in dimethoxyethane with 0.1 M tetrabutylammonium perchlorate. For comparison, the related compounds 11 and 12 were also examined, as well as phenanthrenequinone (13). Since some of the reduction products are expected to be kinetically unstable, we have used the technique of second-harmonic a.c. polarography,[13] at a dropping mercury electrode, which can give reversible potentials even with very unstable systems.[14] In all cases we observed good reversible behavior, and the crossing point reversible potential could be determined within 5 mV. The results are displayed in the table.

Compound	E_1[a,b]	E_2	$E_1 + E_2$
11	-1.22	-1.92	-3.14
12	-1.17	-1.87	-3.04
3	-0.97	-1.47	-2.44
13	-0.73	-1.34	-2.07

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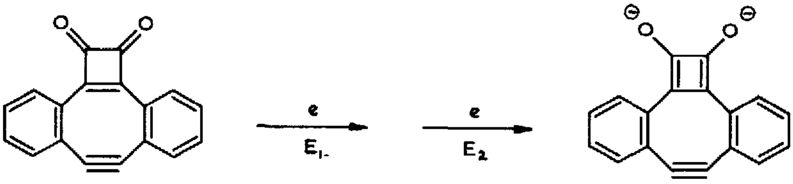
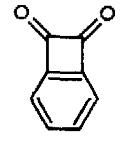
a. Determined by second harmonic a.c. polarography[13,14] at a dropping mercury electrode in dimethoxyethane 0.1 M in tetrabutylammonium perchlorate.

b. Volts versus Ag/AgCl reference electrode.



3 10



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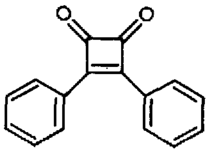

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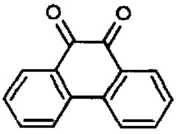

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The sum of the two potentials, $E_1 + E_2$, reflects the total energy change on conversion of the quinone to the conjugated dianion. As expected,[15] reduction of 11 and 12 are thermodynamically difficult since the products are cyclobutadienes (although reduction of 11 is not easier[16] than reduction of 12, as might have been expected on this basis). By contrast, reduction of 13 produces a stable benzene ring, and is easy.

The interesting observation is that reduction of 3 is also rather easy, with a total energy change closer to that for the aromatic case 13 than for the antiaromatic cases 11 and 12. The models may not perfectly mirror the effects of the benzene rings in 3, or small inductive effects. However, it is difficult to escape the conclusion that fusion of the two antiaromatic 4n π electron rings in 10, whose core is a cyclobutadienocyclooctatetraene π system, has resulted in stabilization. In such a system the two component 4n π systems are fused into an overall 4n + 2 π electron periphery.

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References and Notes

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7. Isolated by layer chromatography on Merck Kieselgel 60 PF_{254}.
8. The ^1H nmr, ir, and electronic spectra, as well as the high resolution mass spectrum and/or elemental analysis, were in accord with the assigned structure.
9. See M.P. Cava and R. Muth, J. Org. Chem., 27, 757 (1962); M.P. Cava, D.R. Napier, and R.J. Pohl, J. Amer. Chem. Soc., 85, 2076 (1963).
10. The exact yield of 3 could not be determined, due to its instability.
11. The ε values are minimum ones, due to the instability of 3.
12. By comparison, the olefinic protons in the ^1H nmr spectrum of compound 2, in which the eight-membered ring is paratropic, resonate at τ 4.50 (ref. 3).
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16. This is perhaps not surprising, since the total conjugated system to which the electron is being added is much smaller in 11 than in the other compounds. Differences in the total size of the conjugated system may also make a minor contribution to some of the other observed reduction potentials.