8,11-Dihydropleiadene-8,11-dione. A New Pleiadenequinone with Considerable Electron Affinity

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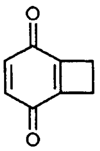
The title compound **2**, is synthesised *via* the valence isomer **6** and shows an electron affinity comparable to *p*-benzoquinone; it also has potential synthetic utility for dienes.

Among 24 possible isomers of dihydropleiadenedione (pleiadenequinone), only 7,12-dihydropleiadene-7,12-dione **1**[1] is known. Although **1** is formally a quinone of pleiadene, it behaves like a normal diaryl ketone owing to its strong local aromatic nature.[2] As a part of our studies on novel quinonoid compounds, we have synthesised 8,11-dihydropleiadene-8,11-dione **2**, the second isomer synthesised in the pleiadenequinone series, which shows appreciably low reduction potentials comparable to *p*-benzoquinone.

Scheme 1 depicts the synthesis of **2**. Photochemical cycloaddition of 2-cyclohexene-1,4-dione **3**[3] and acenaphthylene (1.5 equiv.) in dichloromethane gave the [2 + 2] adduct **4** (m.p. 170–171 °C) in 15% yield in addition to large amounts of acenaphthylene dimers.[4] Attempts to improve the yield of **4** were unsuccessful owing to the facile dimerisation of acenaphthylene and precipitation of the dimers during photolysis. The stereochemistry of **4** is assigned to be *cis-trans-cis* by analogy with other [2 + 2] adducts of **3**.[5] Oxidation of **4** to the enedione **5** (m.p. 180–181 °C, 60%) with selenium dioxide, enolisation with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and subsequent oxidation with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) afforded the cyclobutaquinone **6**† in 67% yield as orange crystals (m.p. 193 °C decomp.). Upon heating at 180 °C in *o*-dichlorobenzene for 15 min, **6** underwent smooth valence isomerisation to furnish the desired pleiadenequinone **2**† in 85% yield as dark violet



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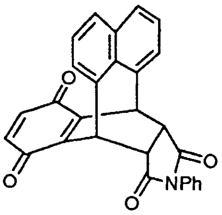

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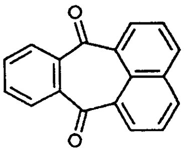

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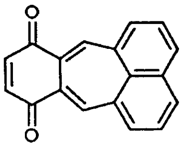

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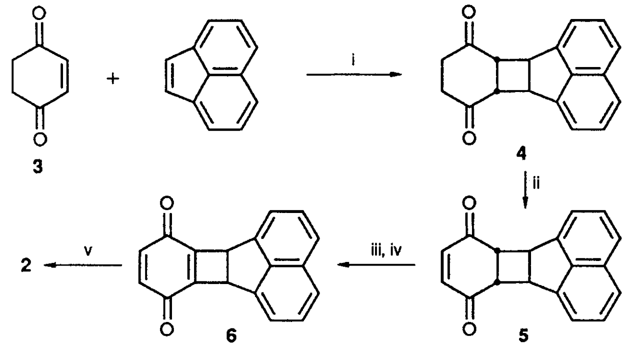
† *Selected spectroscopic data* for **2**: ^{1}H NMR ($CDCl_3$) δ 6.96 (s, H-9, 10), 7.13 (dd, *J* 8.0, 1.5 Hz, H-1, 6), 7.19 (t, *J* 8.0 Hz, H-2, 5), 7.36 (s, H-7, 12), 7.46 (dd, *J* 8.0, 1.5 Hz, H-3, 4); ^{13}C NMR ($CDCl_3$) δ 127.2 (C-2, 5), 129.1 (C-7a, 11a), 132.0 (C-3, 4), 135.3 (C-1, 6), 135.7 (C-6a, 12a), 137.3 (C-3a), 138.2 (C-3b), 140.9 (C-9, 10), 147.5 (C-7, 12), 183.1 (C-8, 11); UV (EtOH) λ_{max} (ε) 239 (20 600), 256 (20 400), 315 (2 680), 343 sh (2 050), 481 nm (5 450); IR (KBr) ν 1672, 1620, 1576, 1304, 854, 768 cm^{-1}. **6**: ^{1}H NMR ($CDCl_3$) δ 5.19 (s, 2H), 6.64 (s, 2H), 7.24–7.80 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 53.2, 122.1, 124.9, 128.3, 132.7, 136.7, 137.9, 139.2, 152.6, 182.5; UV (EtOH) λ_{max} (ε) 257 (12 200), 278 (7 780), 289 (8 500), 300 (5 660), 343 (500), 399 (420), 510 nm (260); IR (KBr) ν 1668, 1640, 1608, 1332, 850, 818, 787 cm^{-1}.

Table 1 Reduction potentials of quinones[a]

Compound	$E_{1/2}(I)$[b]	$E_{1/2}(II)$[b]	$\Delta E_{1/2}$[c]
p-Benzoquinone	−0.63	−1.25	0.62
7	−0.63	−1.31	0.68
6	−0.52	−1.16	0.64
2	−0.63	−1.01	0.38
1	−1.45	−1.84	0.39

[a] Measured by cyclic voltammetry, in MeCN using Et_4NClO_4 (0.1 mol dm^{-3}) as electrolyte. [b] In V *vs.* saturated calomel electrode. [c] $E_{1/2}$(I) − $E_{1/2}$ (II), in V.



Scheme 1 *Reagents and conditions*: i, *hν*, Pyrex filter, CH_2Cl_2, 10 h; ii, SeO_2, dioxane, reflux, 1.5 h; iii, DBU, THF, room temp.; iv, DDQ, acetone, room temp.; v, 180 °C, *o*-dichlorobenzene, 15 min

crystals (m.p. 202 °C decomp.). Prolonged heating led to a decrease in the yield owing to decomposition of **2**.

The absorption spectrum of **6** shows a weak maximum at λ_{max} 510 nm (ε 260) which is absent in the spectra of naphthalene and the parent cyclobutaquinone **7**.[6] This suggests the existence of some through-bond or through-space interaction between the *p*-benzoquinone and 1,8-perinaphthyl groups. The V-shaped geometry of **6** makes through-space interaction feasible with the favorable HOMO–LUMO relationship (HOMO of naphthalene *vs.* LUMO of *p*-benzoquinone). On the other hand, **2** exhibits a considerably intense absorption in the visible region [λ_{max} 481 nm (ε 5500)], which can be ascribed to a π, π* transition (CNDO/S* calculation). Thus, the new pleiadenequinone **2** constitutes quite a different π-electron system from the colourless **1**.

Upon electrochemical reduction (cyclic voltammetry, Table 1), the cyclobutaquinone derivative **6** [$E_{1/2}$(I) = −0.52 V] is reduced more readily than **7** [$E_{1/2}$(I) = −0.63 V], probably reflecting the homoconjugation. The new pleiadenequinone **2** has essentially the same value of $E_{1/2}$(I) (−0.63 V) as that of *p*-benzoquinone and **7**. Accordingly, **2** has appreciably high electron affinity comparable to *p*-benzoquinone in sharp contrast with the low electron affinity of **1**.

The quinone **2** behaves as a diene: reaction of **2** with *N*-phenylmaleimide at 160 °C in *o*-dichlorobenzene afforded the Diels–Alder adduct **8** in 82% yield (m.p. 260 °C decomp.). Thus, **2** should promise the synthesis of a variety of three dimensional π-electron systems containing *p*-benzoquinone and 1,8-perinaphthyl group.

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