2,3,4,5,6,7,9,10,11,12,13,14-Dodecahydro-7,14-dimethylene-1*H*,8*H*-tetracyclopent[*a*,*c*,*h*,*j*]anthracene: a Stable *p*-Quinodimethane

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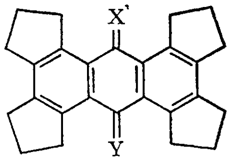
THEORETICAL STUDIES indicate that quinodimethanes which lack substituents on the methylene groups should be highly reactive.[1] This is supported by unsuccessful attempts to isolate simple examples, polymers or dimers being the usual products in such cases.[2] Recently Dickerman and his co-workers have reported the isolation and characterisation of two stable *p*-quinodimethanes with unsubstituted methyl groups, the 1,4,5,8-tetraphenyl and 1,4-diphenyl derivatives of 9,10-dihydro-9,10-dimethyleneanthracene,[3] which have u.v. maxima at 273 nm., in apparent agreement with the predicted value of 275 nm. for 9,10-dihydro-9,10-dimethyleneanthracene (I).[4] Whilst the correspondence between theoretical and experimental values seems good, these compounds are polyphenyl-substituted unsaturated species and as such contain a complex-extended conjugated system whose u.v. and visible absorption bands are difficult to interpret unambiguously. We have prepared a third stable anthraquinodimethane with unsubstituted methylene groups, (II), which does not have this complication, and report its u.v. spectrum together with that of the corresponding quinone methide (III) and quinone (IV).



(II) $X=Y=CH_2$
(III) $X=CH_2$, $Y=O$
(IV) $X=Y=O$

Addition of methyl-lithium in ether solution to the quinone (IV)[5] in benzene–ether yields a diol,†

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† Elemental analyses of all new compounds were satisfactory.

[90%, m.p. 277—278° decomp. ν_{max} (Nujol) 3500 and 1130 cm.$^{-1}$] readily dehydrated in benzene–methanol solution by hydrogen iodide to give a white crystalline solid [82%, m.p. 270—280° decomp. ν_{max} ($CHCl_3$) 3050, 1618, and 899 cm.$^{-1}$; λ_{max} (cyclohexane) 223 nm. (log ϵ 4·66), 254 (4·47), and 283 (4·25); τ ($CDCl_3$) 4·53 (s, 4H), 6·98 (t, J 7Hz, 8H), 7·26 (t, J 7Hz, 8H), and 8·04 (quintet, J 7Hz, 8H)]. Structure (II) is fully consistent with these properties. The compound is stable in the solid state at room temperature, and its u.v. spectrum in cyclohexane remains unchanged after the solution has been heated under reflux for 20 hr. in an inert atmosphere.

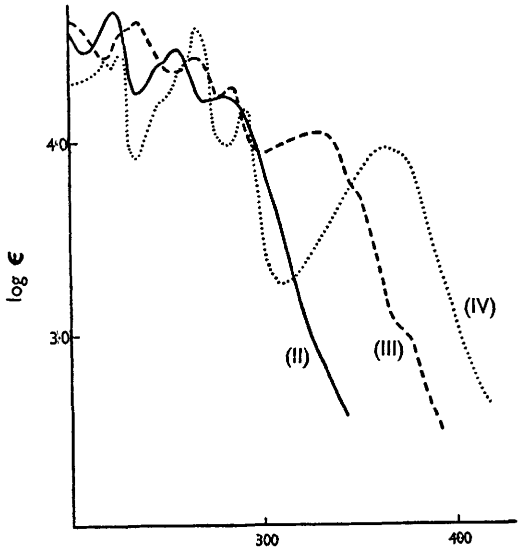

FIGURE. *Ultraviolet absorption spectra of* (II), (——), III), (---), *and* (IV), (. . .) *in cyclohexane.*

In general, *p*-quinone methides are also highly reactive compounds, although a number of relatively stable examples have been reported.[6] In particular, 10-methyleneanthrone appears to be stable under normal conditions.[7] Treatment of the quinone (IV) in benzene–ether with one molar equivalent of methyl-lithium in ether affords a hydroxy-ketone [73%, m.p. 250—251° (decomp.), ν_{max} (Nujol) 3450, 1632, 1568, and 1130 cm.$^{-1}$] which is dehydrated in dimethyl sulphoxide at 170° to give (III), [82%, m.p. 258—259·5° (decomp.), ν_{max} ($CHCl_3$), 3030, 1645, 1573, and 907 cm.$^{-1}$; λ_{max} (cyclohexane) 235 nm. (log ϵ 4·62), 266 (4·47), 284 (4·29), and 330 (4·07); n.m.r. signals at τ ($CDCl_3$) 4·23 (s, 2H), 6·64 (t, J 7Hz, 4H), 6·90 (t, J 7Hz, 4H), 7·22 (m, 8H), and 7·91 (m, 8H)].

The n.m.r. spectrum of the quinodimethane at −50° retains the sharp signal assigned to the vinyl protons but the absorptions corresponding to the methylene protons in the five-membered rings collapse from the well-defined multiplets observed at room temperature, to form broad diffuse bands. By contrast, the signals in the spectrum of the quinone methide, (III), are only slightly broader at −50° than at room temperature. Thus it appears that, like the tetraphenyl derivatives,[3] the quinodimethane (II) is a non-planar molecule. The proximity of the nearest benzylic hydrogen atoms of the five-membered rings does not appear to affect the in-plane and out-of-plane bending vibrations of the unsaturated methylene groups, which have normal frequencies. However this structural feature could be responsible for the largest fragment in the mass spectrum (8% of the molecular ion) corresponding to the loss of methane. Associated with the molecular ion are isotope peaks of the expected intensity for the molecular formula $C_{28}H_{28}$. Similar confirmation of molecular formula is obtainable from the mass spectrum of the quinone methide.

The u.v. spectrum of the quinodimethane (II) (Figure) shows a band at 283 nm., which is the same value as that observed for a solution of the unsubstituted hydrocarbon, 9,10-dihydro-9,10-dimethyleneanthracene[2d] and in good agreement with the value of 275 nm. theoretically predicted.[4] The quinone methide (III) has a band maximum at 284 nm. whereas 10-methyleneanthrone is reported to absorb at 273 nm.[7b] The substituent effect of the fused five-membered rings on the "quinonoid" absorption of the quinone,[8] quinone methide, and quinodimethane (see Table) is thus readily interpreted in terms of electron release[9] from the substituents to the parent systems, whose electron affinities would be expected to decrease in the above order.

Ultraviolet maxima of quinonoid bands and substituent effect (nm.)

	Quinone	Quinone methide	Quinodimethane
Unsubstituted ..	271 (VI)	273 (V)	283 (I)
Substituted ..	290 (IV)	284 (III)	283 (II)
Shift	19	11	0

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