Autoxidation of a Sterically Hindered Phenanthrene-4,5-diol and Conversion of the Products into Phenanthrenequinones

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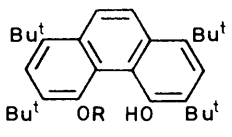
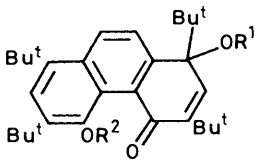
1,3,6,8-Tetra-t-butylphenanthrene-4,5-diol (**1**) is surprisingly susceptible to autoxidation to the hydroperoxide (**2**), the crystal structure of which has been determined. This reaction is initiated by light. In turn, the hydroperoxide (**2**) undergoes acid-catalysed autoxidation to the bishydroperoxide (**12**). The conversion of these hydroperoxides into the quinones (**14**) and (**15**) is described, as well as the autoxidation of some related phenanthrols. The ease of autoxidation is attributed to severe steric crowding in the bay region.

In the previous paper[1] we described the preparation of the phenanthrene-4,5-diol (**1**), noting its extreme sensitivity to air. Although showing no sign of change under argon over a period of eighteen months, solutions in chloroform exposed to the air for only a few minutes became red and when concentrated yielded over 80% of the red hydroperoxide (**2**).



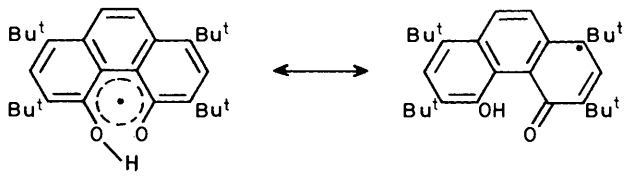
(**1**) R = H
(**3**) R = Me



(**2**) R^1 = OH, R^2 = H
(**4**) R^1 = R^2 = H
(**5**) R^1 = OH, R^2 = Me

On the basis of spectroscopic measurements it was not easy to decide between structure (**2**) and the alternative 3-hydroperoxy, linearly conjugated enone. Thus, the u.v. absorption maximum at 281 nm is midway between calculated values[2] for linearly and cross-conjugated dienones. Similarly, the ^{13}C n.m.r. chemical shift of the carbonyl carbon at δ 196.1 is midway between reported[3] values. However, the chemical shift of the sp^3 carbon attached to the hydroperoxy group (δ 88.5) is more consistent with that of a cross-conjugated dienone; typically at lower field. The unusually low i.r. carbonyl absorption at 1 625 cm^{-1}, clearly the result of intramolecular hydrogen-bonding in the bay region, gave no clue as to the type of conjugation. This ambiguity was resolved in favour of structure (**2**) by crystal structure determination.

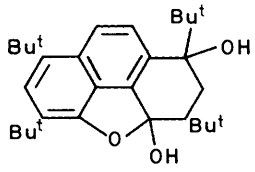
Phenols are characteristically subject to autoxidation in alkaline solution,[4] but reaction with oxygen, catalysed by radical initiators, also occurs in neutral media,[5] as does reaction with singlet oxygen.[6] To clarify the mechanism involved in this remarkably facile oxidation of the diol (**1**), various experiments were carried out. No oxidation occurred when air was bubbled through the solution in the dark. Light is therefore necessary. Solutions of the diol (**1**) were then exposed to limited quantities of air and light in the presence of either t-butylhydroquinone, a radical inhibitor, or 1,4-diazabicyclo[2.2.2]octane (DABCO), a singlet oxygen quencher, and compared, using n.m.r. spectroscopy, with a control containing no additive. All three solutions rapidly discoloured. Spectra of the control sample soon showed broadened resonances, consistent with the presence of radicals, and the appearance of signals due to the hydroperoxide (**2**). A similar rate of oxidation was observed for the sample containing DABCO, but t-butylhydroquinone efficiently inhibited the oxidation. Appreciable amounts of the hydroperoxide were only detected after an hour, by which time *ca.* 50% conversion had been observed in the other samples. These results are consistent with an autoxidation involving free radical intermediates, but not with a self-sensitized singlet oxygen photo-oxidation. Initiation by photochemically produced radicals from chloroform, although possible in this solvent, appeared unlikely, as the autoxidation proceeded equally well in benzene. It appears, therefore, that initiation must be the result of photochemical homolysis of an O–H bond of the diol, as established by Porter *et al.*[7] for phenol itself. The appearance of a strong signal, although without hyperfine splitting, when a degassed benzene solution of the diol (**1**) was irradiated in the cavity of an e.s.r. spectrometer, supports this. The quite remarkable ease of autoxidation of (**1**) must be due to severe steric crowding of the hydroxy groups in the bay region. Abstraction of one hydrogen atom presumably results in a hydrogen-bridged radical (**6**) similar to those observed on oxidation of various biphenyl-2,2′-diols,[8] but more strained. A greater release of strain may be achieved by localization of the unpaired electron of C-1 and/or C-3, as in (**7**), where the enone ring can become puckered. The observed preference for attack by oxygen at C-1 may be the result of thermodynamic or steric factors. The colour of the hydroperoxide (**2**) is surprising, and indicates a degree of charge transfer.



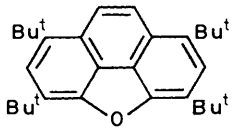
(**6**) (**7**)

Catalytic hydrogenation, reduction with triphenylphosphine, or attempted reductive acetylation of the hydroperoxide (**2**) all gave the alcohol (**4**), whose only substantial spectroscopic difference from (**2**) was in the n.m.r. chemical shift of the vinyl proton at C-2. On the other hand, with sodium borohydride the hydroperoxide (**2**) gave a colourless product believed to be the diol (**8**) in spite of the somewhat deshielded aliphatic t-butyl resonances at δ 1.24 and δ 1.22 in the n.m.r. spectrum. Other spectroscopic data were in complete agreement with this formulation, as was the compound's facile dehydration to the furan (**9**). N.m.r. spectra of aged solutions of (**8**) showed some evidence of opening of the hemiacetal ring to the hydroxy ketone tautomer, but this never exceeded 10% and the tautomer could not be isolated.

N.m.r. samples of the hydroperoxide (**2**) in deuteriochloroform gradually faded in the light, the spectra simplifying to that



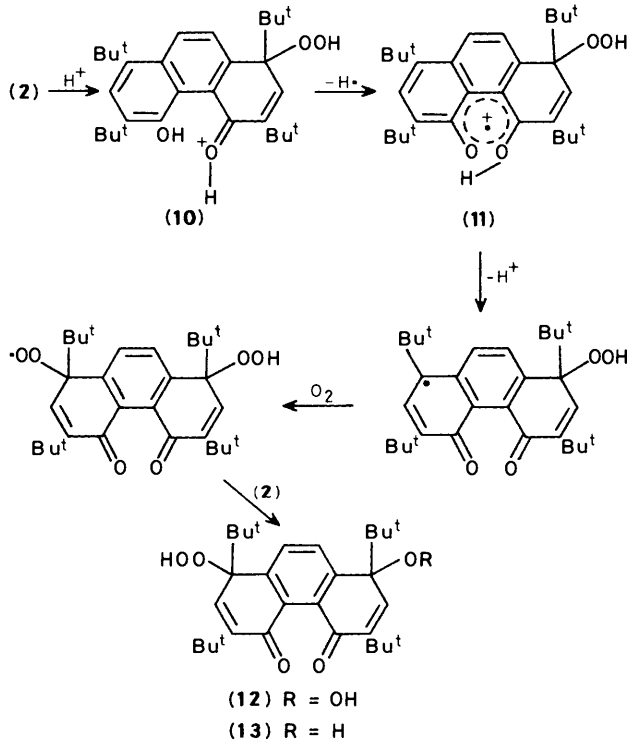
(8)



(9)

of a symmetrical molecule, namely the bishydroperoxide (**12**), and the other spectroscopic data supported this structure. This second oxidation was much slower than the first, requiring irradiation for some 20 h for completion. It was even slower in carbon tetrachloride, and it soon became apparent that deuterium chloride, produced on irradiation of the solvent deuteriochloroform, was a necessary catalyst. The need for acidic catalysis was demonstrated on finding that autoxidation could be achieved by irradiation of compound (**2**) in a variety of solvents to which a trace of toluene-*p*-sulphonic acid had been added.

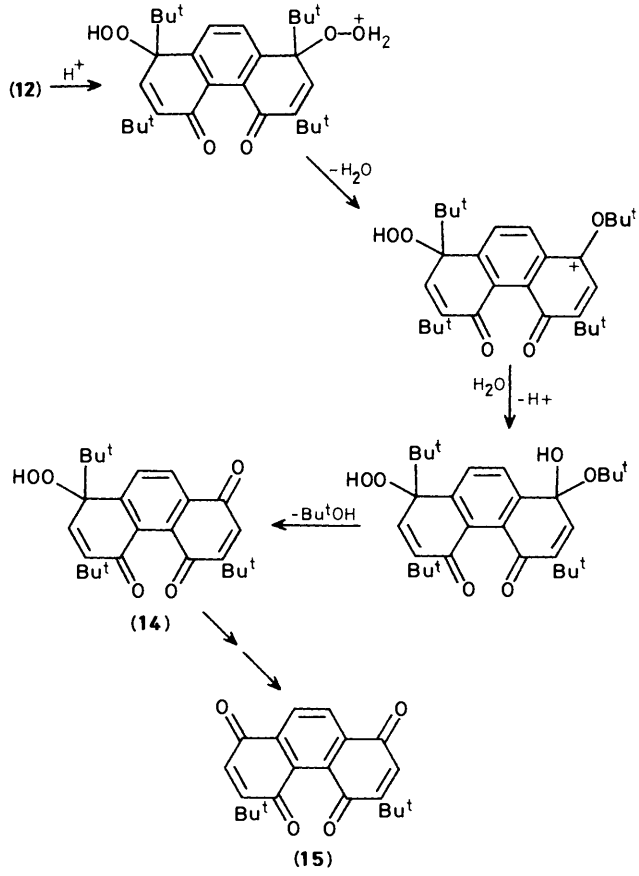
The phenolic hydrogen of the hydroperoxide (**2**) is strongly hydrogen bonded to the carbonyl oxygen, and does not exchange with deuterium oxide until a trace of trifluoroacetic acid has been added. Thus, in the absence of acid, abstraction of the phenolic hydrogen atom would be difficult. Protonation of the carbonyl group, as in (**10**), should decrease the strength of the hydrogen bond, and facilitate hydrogen abstraction to give the radical cation (**11**) as shown in Scheme 1. Inhibition of autoxidation by hydrogen bonding has previously been noted by Brady *et al.*[9]



Scheme 1.

Like compound (**2**) the reduction product (**4**) was also susceptible to autoxidation, and on attempted recrystallization of (**4**) from dichloromethane the hydroxy hydroperoxide (**13**) was formed. This is not surprising, and the reaction was not studied in any detail.

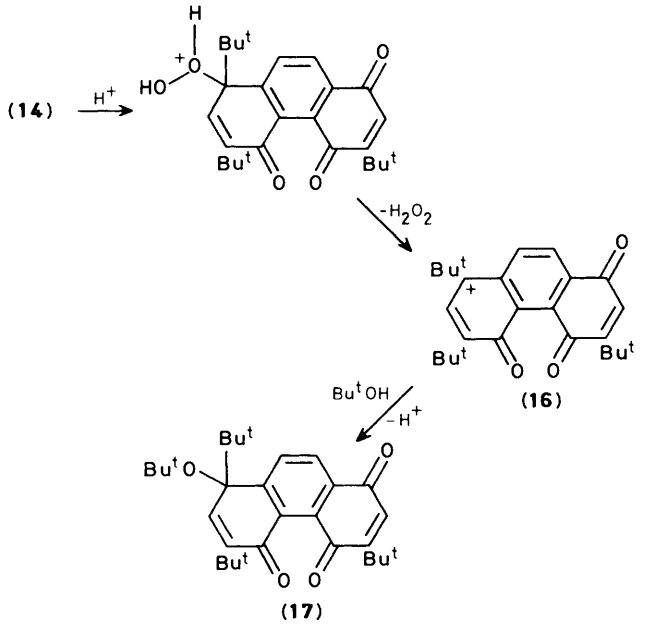
On prolonged contact with acid the bishydroperoxide (**12**) decomposed. The two major products were the hydroperoxyquinone (**14**) (15%) and the previously described[10] diquinone (**15**) (55%). Although a satisfactory combustion analysis could not be obtained for the hydroperoxide, both spectroscopic and chemical evidence support structure (**14**). Thus, the n.m.r. spectrum showed only three t-butyl groups and one hydroperoxy proton as compared to that of (**12**). On one occasion a third product was isolated and identified as the t-butyloxy quinone (**17**). The ^{13}C n.m.r. spectrum is consistent with this structure, the main features being three carbonyl resonances and two signals near 80 p.p.m. for C-1 and the tertiary carbon of the t-butoxy group. The mass spectra of both (**14**) and (**17**) showed a number of ions near mass 350, indicating easy breakdown to the diquinone (**15**). Scheme 2, showing the



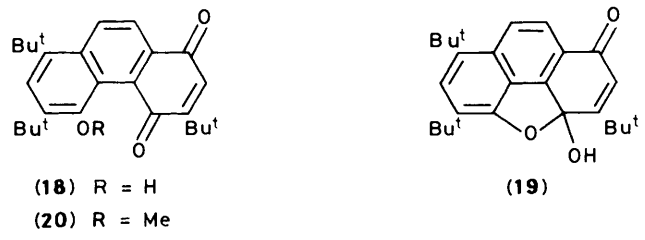
Scheme 2.

formation of products (**14**) and (**15**), is based on the normal acid-catalysed rearrangement of hydroperoxides[11] with, in this case, preferential migration of the t-butyl group.[12] The formation of the t-butoxy compound (**17**) can be explained by protonation of the alternative hydroperoxy oxygen atom[12] of the quinone (**14**) as in Scheme 3, followed by loss of hydrogen peroxide and trapping of the resulting cation (**16**) by liberated t-butyl alcohol.

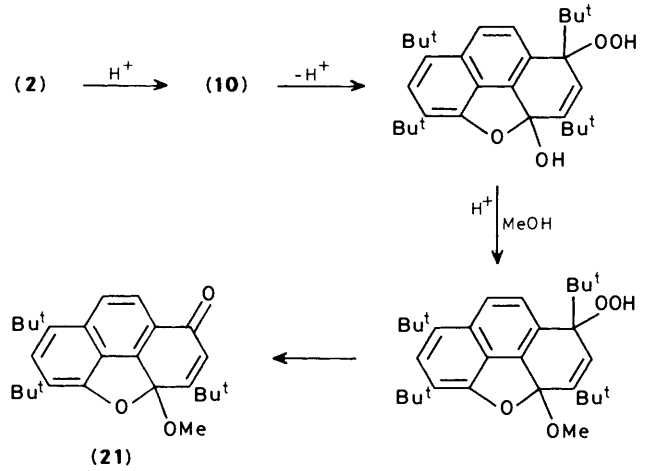
As both the hydroperoxyquinone (**14**) and the bishydroperoxide (**12**) had been converted into other products on treatment with acid, it was surprising that the hydroperoxide (**2**) had not. Attempts merely led to autoxidation. When oxygen was excluded the hydroperoxide (**2**) decomposed in chloroform or ethyl acetate containing a little toluene-*p*-sulphonic acid, but none of the expected product, the hydroxyquinone (**18**) or its tautomer (**19**) could be isolated, although the mixture became reddish-purple.



Scheme 3.



In a mixture of methanol and acetic acid, however, a 30% yield of the acetal (**21**) [δ(OMe) 3.06] was produced. As the solution remained yellow throughout the reaction, the hydroxyquinone (**18**), if involved, must rapidly tantomerize or react further under these conditions. Alternatively, preferential protonation of the bay region carbonyl may occur, forming (**10**) as in the autoxidation, followed, in the absence of oxygen, by acetal formation and subsequent loss of t-butyl alcohol (Scheme 4).



Scheme 4.

Finally, the monomethyl ether (**3**) of the diol (**1**) was also found to be susceptible to autoxidation, giving the hydroperoxide (**5**), whose structure is based on spectroscopic data and its acid-catalysed transformation to the methoxyquinone (**20**). In contrast to the hydroxyquinone (**18**) this compound was quite stable and could also be prepared by oxidation of the phenol (**3**) with dichromate.

Experimental

General methods are given in the previous paper.[1] Deuteriochloroform and carbon tetrachloride solutions were used for n.m.r. and i.r. measurements, respectively.

1-*Hydroperoxy*-5-*hydroxy*-1,3,6,8-*tetra*-t-*butylphenanthren*-4(1H)-*one* (**2**).—Lithium aluminium hydride (60 mg) was added to a stirred solution of 1,3,7,9-tetra-t-butylphenanthro[4,5-*def*][1,3,2]dioxathiepine 5-oxide (197 mg), prepared as described in ref. 1, in dry tetrahydrofuran (10 ml) under nitrogen. After 30 min, dilute sulphuric acid was added dropwise, the product was extracted with ether, and the combined extracts were washed with water. Evaporation of the dried extract left an off-white foam which was taken up in chloroform (3 ml). The solution was swirled in the air for a few minutes whereupon it turned deep orange-red. Evaporation followed by crystallization of the residue from light petroleum gave red crystals of the *hydroperoxide* (**2**) (158 mg, 83%), m.p. 151—153 °C (decomp.) (Found: M^+, 466.313. $C_{30}H_{42}O_4$ requires M, 466,308); m/z 466 (2%) and 377 (100, $M^+ - C_5H_{13}O$); $\nu_{max.}$ 3 540, 3 520, 3 260br (OH), and 1 625 cm^{-1} (CO); $\lambda_{max.}$(hexane) 412 (log ε 3.16), 281 (3.83), and 216 nm (4.13); δ_H 0.98 (9 H, s, Bu^t), 1.41 (9 H, s, Bu^t), 1.54 (9 H, s, Bu^t), 1.63 (9 H, s, Bu^t), 7.14 (1 H, s, vinyl H), 7.65 (1 H, s, OOH), 7.70, 8.71 (2 H, AB system, J 9.7 Hz, ArH), 7.72 (1 H, s, ArH), and 8.73 (1 H, s, ArOH); δ_C 196.1 (C-4).

Reduction of the Hydroperoxide (**2**).—(*a*) *By hydrogenation.* The hydroperoxide (**2**) (12 mg) was hydrogenated in ethanol (5 ml) over 10% palladized charcoal (1 mg), requiring 1 mol equiv. of hydrogen. The catalyst was filtered off through Celite and the filtrate was evaporated to give 1,5-*dihydroxy*-1,3,6,8-*tetra*-t-*butylphenanthren*-4(1H)-*one* (**4**) (11 mg) which decomposed on attempted recrystallization (Found: M^+, 450.311. $C_{30}H_{42}O_3$ requires M, 450.313); m/z 450 (5%), 394 (74), 338 (71), 323 (66), and 57 (100); $\nu_{max.}$ 3 620, 3 200br (OH), and 1 635 cm^{-1} (CO); δ_H 0.99 (9 H, s, Bu^t), 1.38 (9 H, s, Bu^t), 1.54 (9 H, s, Bu^t), 1.62 (9 H, s, Bu^t), 2.14 (1 H, s, OH), 6.91 (1 H, s, vinyl H), 7.71 (1 H, s, ArH), 7.79, 8.64 (2 H, AB system, J 9.2 Hz, ArH), and 8.88 (1 H, s, ArOH).

(*b*) *With triphenylphosphine.* Using the procedure of Bartlett *et al.*[13] triphenylphosphine (20 mg) was added to a solution of the hydroperoxide (**2**) (32 mg) in benzene (0.5 ml). The mixture was heated at 55 °C for 20 h whereupon rapid silica chromatography of the crude product gave the diol (**4**) (30 mg). On attempted crystallization from benzene–light petroleum this material decomposed. Preparative t.l.c. gave the diol (**4**) (10 mg) and 1-*hydroperoxy*-8-*hydroxy*-1,3,6,8-*tetra*-t-*butylphenanthrene*-4,5(1H,8H)-*dione* (**13**) (5 mg) as a pale yellow gum [Found: ($M^+ - C_8H_{18}O$) 352.160. $C_{22}H_{24}O_4$ ($M^+ - C_8H_{18}O$) requires 352.167]; m/z 354 (24%), 353 (24), 353 (31), 352 (100), and 337 (58); $\nu_{max.}$ 3 590, 3 510 (OH), 1 680, 1 670 (C=O), and 1 620 cm^{-1} (C=C); δ_H 0.89 (9 H, s, Bu^t), 0.93 (9 H, s, Bu^t), 1.38 (9 H, s, Bu^t), 1.39 (9 H, s, Bu^t), 2.14 (2 H, br s, OH), 6.65 (1 H, s, vinyl H), 6.68 (1 H, s, vinyl H), and 7.66 and 7.77 (2 H, AB system, J 8.5 Hz, ArH).

(*c*) *With sodium borohydride.* Sodium borohydride (15 mg) was added to a stirred solution of the hydroperoxide (**2**) (61 mg) in ethanol (5 ml). After 16 h the mixture was poured into water

and extracted with ether. The extract was washed with water, dried, and concentrated to give 1,3,5,7-*tetra-t-butyl*-1,2,3,4-*tetrahydrophenanthro*[4,5-bcd]*furan*-1,3a-*diol* (**8**) (57 mg, 96%), m.p. 204—206 °C (from dichloromethane–light petroleum) (Found: M^+, 452.335. $C_{30}H_{44}O_3$ requires M, 452.329); m/z 452 (13%), 395 (100, $M^+ - C_4H_9$); $\nu_{max.}$ 3 600 and 3 590 cm^{-1} (OH); δ_H 1.22 (9 H, s, Bu^t), 1.24 (9 H, s, Bu^t), 1.46 (9 H, s, Bu^t), 1.55 (9 H, s, Bu^t), 1.75—2.14 (2 H, m, 2-H), 2.60—3.09 (1 H, m, 3-H), 2.83 (2 H, s, OH), 7.38 (1 H, s, ArH), and 7.60 and 8.10 (2 H, AB system, J 9.2 Hz, ArH).

A solution of the diol (**8**) (11 mg) in ethyl acetate (1 ml) was treated with toluene-*p*-sulphonic acid (2 mg). After 18 h crystalline 1,3,5,7-tetra-t-butylphenanthro[4,5-*bcd*]furan (**9**) (8 mg, 80%) was filtered off. It had m.p. 320 °C (sealed tube) (lit.,[1] 320 °C).

Autoxidation of the Hydroperoxide (**2**).—(*a*) A solution of the hydroperoxide (**2**) (150 mg) in chloroform (10 ml) was irradiated with an incandescent lamp for 19 h. T.l.c. of the residue obtained on evaporation of the reaction mixture afforded 8-*hydroperoxy*-5-*oxo*-3,6,8-*tri-t-butyl*-5,8-*dihydrophenanthrene*-1,4-*quinone* (**14**) (24 mg, 18%), m.p. 165—167 °C (decomp.) (from dichloromethane–light petroleum) [Found: ($M^+ - O_2$), 392.234. $C_{26}H_{32}O_3$ requires ($M^+ - O_2$), 392.235]; m/z 392 (8%), 352 (34), 351 (100), and 350 (54); $\nu_{max.}$ 3 550, 3 400br (OOH), 1 680, and 1 665 cm^{-1} (CO); $\lambda_{max.}(CH_2Cl_2)$ 338 (log ε 3.11), 259 (4.17), and 250sh nm, (4.12); δ_H (0.91 (9 H, s, Bu^t), 1.41 (9 H, s, Bu^t), 1.42 (9 H, s, Bu^t), 6.70 (1 H, s, vinyl H), 6.90 (1 H, s, vinyl H), 7.81 (1 H, br, OOH), and 7.84 and 8.09 (2 H, AB system, J 8.0, ArH); 3,6-di-t-butylphenanthrene-1,4,5,8-diquinone (**15**), (35 mg, 31%), m.p. 231—232 °C (lit.,[10] 229—229.5); and the yellow 5-*oxo*-8-*t-butoxy*-3,6,8-*tri-t-butyl*-5,8-*dihydrophenanthrene*-1,4-*quinone* (**17**) (23 mg, 15%), m.p. 130—134 °C from methanol [Found: ($M^+ - C_5H_{12}$) 392.200. $C_{25}H_{28}O_4$ requires ($M^+ - C_5H_{12}$) 392.199]; m/z 392 (13%), 353 (12), 352 (57), 351 (39), and 350 (100); $\nu_{max.}$ 1 680 and 1 660 cm^{-1} (CO); $\lambda_{max.}$(MeOH) (log ε) 337 (3.48), 260 (4.46), and 208 nm (4.40); δ_H 0.90 (9 H, s, Bu^t), 1.25 (9 H, s, OBu^t), 1.41 (18 H, s, Bu^t), 6.68 (1 H, s, vinyl H), 6.87 (1 H, s, vinyl H), and 7.81 and 8.03 (2 H, AB system, J 8.3 Hz, ArH).

(*b*) *With oxygen and toluene*-p-*sulphonic acid.* A solution of the hydroperoxide (**2**) (32 mg) and toluene-*p*-sulphonic acid (2 mg) in ethyl acetate (1.5 ml) was set aside for 4 days. The solution was then washed with water, dried, and evaporated, and the residue was subjected to t.l.c. to give the hydroperoxy quinone (**14**) (4.5 mg, 15%), and 1,8-*bishydroperoxy*-1,3,6,8-*tetra-t-butylphenanthrene*-4,5(1H,8H)-*dione* (**12**) (18 mg, 53%), m.p. 133—135 °C, from dichloromethane–light petroleum [Found: ($M^+ - C_4H_9O$), 425.230. $C_{26}H_{33}O_5$ requires ($M - C_4H_9O$), 425.233]; m/z 466 (1%), 352 (100), 351 (78), and 350 (60); $\nu_{max.}$ 3 530 and 3 390br (OOH) and 1 685 and 1 670 cm^{-1} (CO); δ_H 0.91 (18 H, s, Bu^t), 1.40 (18 H, s, Bu^t), 6.87 (2 H, s, vinyl H), 7.72 (2 H, s, ArH), and 7.75 (2 H, br, OOH).

Anaerobic Acid-catalysed Degradation of the Hydroperoxide (**2**).—A solution of the hydroperoxide (**2**) (50 mg) in degassed methanol (3 ml) and acetic acid (1 ml) was set aside under argon for 7 days. The solution was then poured into water and extracted with ether. The extract was washed with aqueous sodium hydrogen carbonate and water before being dried. Evaporation and preparative t.l.c. of the residue afforded 3a-*methoxy*-3,5,7-*tri-t-butylphenanthro*[4,5-bcd]*furan*-1(3aH)-*one* (**21**) (13 mg, 30%), m.p. 170—173 °C, from aqueous ethanol (Found: C, 79.7; H, 8.5. $C_{27}H_{34}O_3$ requires C, 79.8; H, 8.4%); m/z 406 (M^+); $\nu_{max.}$ 1 665 (CO) and 1 600 cm^{-1} (C=C); $\lambda_{max.}$(MeOH) 422 (log ε 3.65), 307sh (4.08), 280 (4.78), 228 (5.12), and 208 nm (4.84); δ_H 1.40 (9 H, s, Bu^t), 1.52 (9 H, s, Bu^t), 1.57 (9 H, s, Bu^t), 3.06 (3 H, s, OMe), 6.12 (1 H, s, vinyl H), 7.51 (1 H, s, ArH), and 7.76 and 8.16 (2 H, AB system, J 8.6 Hz, ArH).

5-*Methoxy*-1,3,6,8-*tetra-t-butylphenanthren*-4-*ol* (**3**).—An ethereal solution of diazomethane was added, under nitrogen, to the diol (**1**) prepared from the cyclic sulphite ester (100 mg) as described for the preparation of (**2**). The following day the residue after evaporation of the ether was purified by t.l.c. and crystallized from aqueous ethanol, to give the monomethyl ether (**3**) (79 mg, 85%), m.p. 279—281 °C (Found: M^+, 448.333. $C_{31}H_{44}O_2$ requires M, 448.334); m/z 450 (4%, $M^+ + 2$), 449 (35, $M^+ + 1$), 448 (100, M^+), and 433 (55); $\nu_{max.}$ 3 250 cm^{-1} (OH); $\lambda_{max.}$(hexane) 376 (log ε 3.20), 338 (3.92), 328 (3.90), 290 (4.06), 257 (4.39), and 216 nm (4.10); δ_H 1.54 (9 H, s, Bu^t), 1.57 (9 H, s, Bu^t), 1.63 (9 H, s, Bu^t), 1.65 (9 H, s, Bu^t), 3.38 (3 H, s, OMe), 7.65 (1 H, s, ArH), 7.69 (1 H, s, ArH), 8.09 and 8.15 (2 H, AB system, J 10.0 Hz, ArH), and 8.83 (1 H, s, OH).

Autoxidation of the Monomethyl Ethyl (**3**).—The monomethyl ether (**3**) (13 mg) in the form of a gum, was left in contact with air for a week. Preparative t.l.c. of this gave unchanged material (2 mg), and 1-*hydroperoxy*-5-*methoxy*-1,3,6,8-*tetra-t-butylphenanthren*-4(1H)-*one* (**5**) (6.5 mg, 47%) [Found: ($M^+ - O$), 464.327. $C_{31}H_{44}O_3$ requires ($M^+ - O$, 464.329]; m/z 464 (7%), 439 (15), 417 (40), 407 (100), 393 (47), and 57 (86); $\nu_{max.}$ 3 530, 3 420br (OOH), and 1 670 cm^{-1} (CO); δ_H 0.94 (9 H, s, Bu^t), 1.47 (9 H, s Bu^t), 1.50 (9 H, s, Bu^t), 1.60 (9 H, s, Bu^t), 3.27 (3 H, s, OMe), 6.96 (1 H, s, vinyl H), 7.58 (1 H, s, ArH), 7.58 and 8.47 (2 H, AB system, J 9.4 Hz, ArH), and 7.64 (1 H, s, OOH).

5-*Methoxy*-3,6,8-*tri-t-butylphenanthrene*-1,4-*quinone* (**20**).—A solution of sodium dichromate dihydrate (60 mg) in water (0.5 ml) and acetic acid (1.0 ml) was added to a stirred suspension of the phenol (**3**) (40 mg) in acetic acid (5 ml). After 14 h the mixture was poured into water and extracted with ether. The extract was washed with aqueous sodium hydrogen carbonate and water, dried, and evaporated. Preparative t.l.c. of the residue, and crystallization from ethanol, furnished the *quinone* (16 mg, 44%), m.p. 167—171 °C (Found: C, 80.0; H, 8.5. $C_{27}H_{34}O_3$ requires C, 79.8; H, 8.4%); m/z 408 (5%, $M^+ + 2$), 407 (23, $M^+ + 1$), 406 (75, M^+), 392 (32) 391 (100), 350 (91), and 349 (86); $\nu_{max.}$ 1 655 cm^{-1} (CO); $\lambda_{max.}$(MeOH) 379 (3.17), 305 (4.25), and 236 nm (4.54); δ_H 1.47 (9 H, s, Bu^t), 1.52 (9 H, s, Bu^t), 1.60 (9 H, s, Bu^t), 3.43 (3 H, s, OMe), 6.70 (1 H, s, vinyl H), 7.70 (1 H, s, ArH), 7.91, and 8.56 (2 H, AB system, J 9.2 Hz, ArH).

This same quinone (**20**) was produced in 95% yield when the hydroperoxide (**5**) was heated under reflux with toluene-*p*-sulphonic acid in ethyl acetate for 6 h.

Structure Determination.—Suitable crystals of the hydroperoxide (**2**) were grown from light petroleum solution. A unique data set was measured to $2\theta_{max.} = 100°$ using a Syntex $P\bar{1}$ four-circle diffractometer in conventional $2\theta/\theta$ scan mode with a nickel-filtered copper radiation source (λ = 1.5418 Å). A total of 2 779 independent reflections were measured, 1 138 with $I > 3\sigma(I)$ being considered 'observed' and used in the 9 × 9 block diagonal least-squares refinement without absorption correction. Anisotropic thermal parameters were refined for C, O; $(x, y, z, U_{iso})_H$ were included constrained at estimated values [exception: the peroxide hydrogen which could not be located from difference maps, probably not being involved in strong hydrogen bonding since the thermal tensor of O(2) is somewhat larger than that of O(1)]. Residuals R,R' on $|F|$ at convergence were 0.066, 0.046. Neutral atom complex scattering factors were used;[14] computation used the XTAL program system[15] implemented by S. R. Hall on a Perkin-Elmer 3240 computer.

Table 1. Non-hydrogen atom co-ordinates

Atom	*x*	*y*	*z*
C(1)	0.027 7(5)	0.698 3(11)	0.739 0(10)
O(1)	−0.029 1(4)	0.675 7(6)	0.660 1(6)
O(2)	−0.060 6(3)	0.579 2(7)	0.705 4(7)
C(100)	0.055 6(5)	0.805 4(9)	0.671 4(10)
C(101)	0.011 8(5)	0.909 3(9)	0.676 5(9)
C(102)	0.060 2(5)	0.776 5(9)	0.533 0(9)
C(103)	0.116 5(5)	0.830 3(10)	0.736 4(11)
C(2)	0.009 3(5)	0.734 5(9)	0.864 9(11)
C(3)	0.044 7(5)	0.713 5(10)	0.969 7(9)
C(30)	0.032 2(5)	0.768 8(10)	1.096 4(9)
C(31)	−0.031 8(5)	0.819 4(9)	1.091 1(9)
C(32)	0.038 9(5)	0.676 6(10)	1.199 4(9)
C(33)	0.080 8(5)	0.865 6(9)	1.127 5(9)
C(4)	0.100 5(5)	0.641 3(10)	0.963 5(10)
O(4)	0.144 0(3)	0.650 4(6)	1.040 5(6)
C(5)	0.098 4(5)	0.552 0(11)	0.860 3(10)
C(6)	0.133 0(5)	0.444 6(10)	0.867 5(11)
C(7)	0.159 2(5)	0.391 1(11)	0.980 3(10)
O(7)	0.144 7(3)	0.434 5(6)	1.093 2(6)
C(8)	0.195 2(5)	0.294 5(10)	0.981 7(10)
C(80)	0.224 8(5)	0.240 1(11)	1.101 8(9)
C(81)	0.176 0(5)	0.192 3(10)	1.181 2(9)
C(82)	0.264 8(5)	0.328 4(11)	1.177 0(11)
C(83)	0.264 2(5)	0.138 0(11)	1.077 4(9)
C(9)	0.203 3(4)	0.244 4(9)	0.864 0(12)
C(10)	0.177 3(5)	0.283 9(10)	0.750 2(10)
C(110)	0.189 2(5)	0.216 4(10)	0.627 7(10)
C(111)	0.130 6(5)	0.164 3(9)	0.563 5(9)
C(112)	0.222 1(5)	0.299 0(10)	0.540 2(9)
C(113)	0.234 6(5)	0.115 7(9)	0.655 6(9)
C(11)	0.140 8(5)	0.385 1(10)	0.750 1(11)
C(12)	0.106 7(5)	0.428 1(11)	0.642 1(10)
C(13)	0.069 0(5)	0.521 3(11)	0.638 3(10)
C(14)	0.065 5(5)	0.586 6(10)	0.750 1(12)

Table 2. Non-hydrogen interatomic distances (see the supplement for the t-butyl geometries)

Atoms	Distance (Å)
C(1)–C(100)	1.58(2)
C(1)–O(1)	1.47(1)
C(1)–C(2)	1.51(2)
C(1)–C(14)	1.53(2)
O(1)–O(2)	1.42(1)
C(2)–C(3)	1.33(1)
C(3)–C(4)	1.49(2)
C(3)–C(30)	1.55(1)
C(4)–C(5)	1.51(2)
C(4)–O(4)	1.21(1)
C(5)–C(6)	1.45(2)
C(5)–C(14)	1.38(2)
C(6)–C(7)	1.43(2)
C(6)–C(11)	1.46(2)
C(7)–C(8)	1.36(2)
C(7)–O(7)	1.38(1)
C(8)–C(9)	1.41(2)
C(8)–C(80)	1.52(1)
C(9)–C(10)	1.37(2)
C(10)–C(11)	1.41(2)
C(10)–C(110)	1.57(2)
C(11)–C(12)	1.41(2)
C(12)–C(13)	1.35(2)
C(13)–C(14)	1.42(2)
O(2)···O(7^{i})[a]	2.99(1)
O(4)···O(7)	2.54(1)

[a] Transformation i is ($\bar{x}$, 1 − *y*, 2 − *z*).

Table 3. Non-hydrogen interbond angles (for t-butyl angles, see the supplement)

Atoms	Angles (°)
C(100)–C(1)–O(1)	102.8(8)
C(100)–C(1)–C(2)	110.3(9)
C(100)–C(1)–C(14)	117.0(9)
O(1)–C(1)–C(2)	106.0(9)
O(1)–C(1)–C(14)	109.1(9)
C(2)–C(1)–C(14)	110.8(9)
C(1)–O(1)–O(2)	111.2(7)
C(1)–C(2)–C(3)	121.3(10)
C(2)–C(3)–C(4)	119.0(10)
C(2)–C(3)–C(30)	121.8(10)
C(4)–C(3)–C(30)	119.0(9)
C(3)–C(4)–C(5)	116.3(9)
C(3)–C(4)–O(4)	121.8(10)
C(5)–C(4)–O(4)	121.7(10)
C(4)–C(5)–C(6)	124.1(9)
C(4)–C(5)–C(14)	114.1(10)
C(6)–C(5)–C(14)	121.4(11)
C(5)–C(6)–C(7)	125.4(11)
C(5)–C(6)–C(11)	117.3(10)
C(7)–C(6)–C(11)	117.3(10)
C(6)–C(7)–C(8)	123.2(10)
C(6)–C(7)–O(7)	118.6(10)
C(8)–C(7)–O(7)	118.1(9)
C(7)–C(8)–C(9)	116.4(10)
C(7)–C(8)–C(80)	123.1(10)
C(9)–C(8)–C(80)	120.5(10)
C(8)–C(9)–C(10)	125.4(10)
C(9)–C(10)–C(11)	117.5(10)
C(9)–C(10)–C(110)	119.4(10)
C(11)–C(10)–C(110)	123.2(9)
C(10)–C(11)–C(6)	119.9(10)
C(10)–C(11)–C(12)	123.2(10)
C(6)–C(11)–C(12)	116.6(10)
C(11)–C(12)–C(13)	125.5(10)
C(12)–C(13)–C(14)	118.4(10)
C(1)–C(14)–C(5)	123.0(11)
C(5)–C(14)–C(13)	120.0(10)
C(1)–C(14)–C(13)	116.8(10)

Relevant results are given in the Figure (which also shows the numbering scheme) and Tables. Non-hydrogen atom thermal parameters, hydrogen atom co-ordinates, and t-butyl geometries have been deposited at the Cambridge Crystallographic Data Centre.*

Crystal Data.—$C_{30}H_{42}O_4$, M = 466.6, monoclinic, space group $P2_1/n$ (C_{2h}^5, no. 14, variant), a = 22.09(1), b = 11.472(7), c = 10.717(5) Å, β = 95.56(4)°, U = 2 702(2) Å^3. D_c (Z = 4) = 1.14 g cm^{-3}. $F(000)$ = 1 016. μ_{Mo} = 3.9 cm^{-1}; specimen: cuboidal fragment, *ca.* 0.2 mm. $T \sim 295$ K.

Structural Commentary.—The results of the structure determination are consistent with the stoicheiometry and connectivity of (**2**) above; a single molecule comprises the asymmetric unit of the structure. The determination is of limited precision in consequence of the small amount of observable data, not all hydrogen atoms being observable in difference maps and whose estimation depends on skeletal assignment. Significant but relatively weak hydrogen bonding in the lattice array is implied by the O(2)···O(7) ($\bar{x}$, 1 − *y*, 2 + *z*) contact of 2.99(1) Å; O(7) is surrounded by the C(3,8) t-butyl arrays and may not

* For details of the CDCC-deposition facility see 'Instructions for Authors (1988),' *J. Chem. Soc., Perkin Trans. 1*, 1988, Issue 1, p. xviii, paragraph 5.6.3.

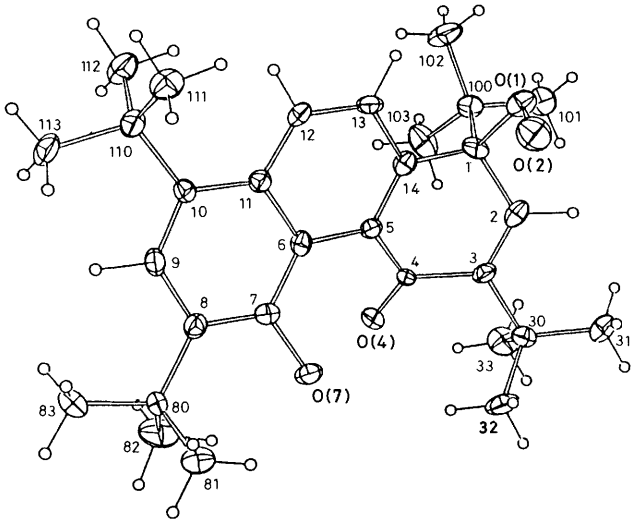


Figure 1. Projection of a single molecule of (**2**); 20% thermal ellipsoids are shown for the non-hydrogen atoms. Hydrogen atoms have arbitrary radii of 0.1 Å. The crystallographic numbering scheme is shown

be easily accessible, and may be intramolecularly hydrogen-bonded to O(4). All angles subtended at O(7) by C(7), O(4,2′) are greater than 90°; C(4)–O(4)···O(7) is 93.2(7)°. The fused ring system of C(5—14) is tolerably planar (χ^2 250), with no atom deviation, δ, greater than 0.12 Å; atom deviations of the other ring are δ C(1—4): 0.07, −0.32, −0.05, and 0.51 Å. δ O(1,4), C(100) are −0.93, 1.18, and 1.41 Å. O(7) is bent well out of plane, in the opposite direction to O(4), by −0.32 Å.

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