# Epoxidation of 1,4-Dihydro-1,4-methanoanthraquinones. Photochemistry and Crystal Structure Determination of the Products

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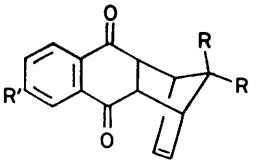
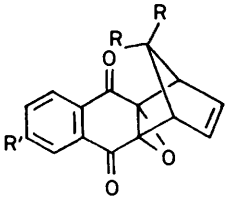
The 1,4-dihydro-1,4-methanoanthraquinones (5), (6), and (10) afforded respectively the pairs of epoxides (2) and (3), (7) and (8), and (11) and (12), on treatment with hydrogen peroxide–aqueous sodium carbonate. When irradiated with sunlight, only one isomer of each pair, *viz.* (3), (8), and (12) underwent rearrangement, giving the quinones (4), (9), and (13) respectively. The stereochemistry of the photolabile epoxides was obtained by a crystal structure determination for the bromo-derivative (11). This was carried out by single-crystal *X*-ray diffraction at 295 K and refined by full-matrix least squares to *R* 0.062 (669 reflections). Crystals are monoclinic, $P2_1/n$, $a$ = 5.870(5), $b$ = 18.13(1), $c$ = 11.475(6) Å, $\beta$ = 95.84(6)°, and $Z$ = 4.

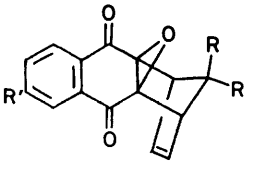
In a preliminary communication we reported [1] that treatment of the naphthoquinone–spirocyclopentadiene adduct (1) [2] with methanolic sodium hydroxide in the presence of air afforded a mixture of two isomeric



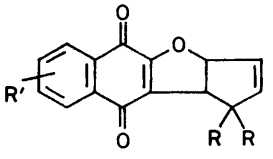
(1) RR = $[CH_2]_2$, R′ = H
(14) R = R′ = H



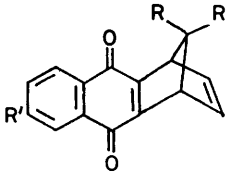
(2) RR = $[CH_2]_2$, R′ = H
(7) R = R′ = H
(11) R = H, R′ = Br



(3) RR = $[CH_2]_2$, R′ = H
(8) R = R′ = H
(12) R = H, R′ = Br



(4) RR = $[CH_2]_2$, R′ = H
(9) R = R′ = H
(13) R = H, R′ = Br



(5) RR = $[CH_2]_2$, R′ = H
(6) R = R′ = H
(10) R = H, R′ = Br

epoxides (2) and (3) as the major products, together with a minor quantity of the quinonoid isomer (4).

It was further shown that on irradiation of the mixture of epoxides in sunlight, or on heating under reflux in methanol or ethanol, one of them rearranged into the quinone (4), while the other remained essentially unchanged. The compound that underwent the isomerisation was tentatively assigned the *endo*-structure (2) on the basis of changes in the chemical shifts of protons of the compounds (2) and (3) on addition of the shift reagent [Eu(fod)$_3$]. However, the availability of several binding sites for the reagent left doubts about the validity of this assignment.

The mixture of epoxides (2) and (3) was most conveniently prepared by epoxidation, with hydrogen peroxide and aqueous sodium carbonate, of the quinone (5), which was in turn obtained from the adduct (1) in two steps.[2]

To assess the generality of the isomerisation of the epoxide (2) or (3) to quinone (4), the quinones (6) [2,3] and (10) were similarly treated with alkaline hydrogen peroxide to afford the epoxide pairs (7) and (8), and (11) and (12). One of each of these pairs of isomers underwent photoisomerisation in sunlight to the quinones (9) and (13). An unequivocal assignment of the stereochemistries of the epoxides undergoing rearrangement was therefore required.

A comparison of the $^1$H n.m.r. spectra of the three pairs of epoxides revealed obvious similarities between the chemical shifts of the photolabile epoxides on the one hand, and between the remaining epoxides on the other (see Table 1), and the conclusion could safely be made that each of the photolabile epoxides has the same stereochemistry. However, attempts to assign the correct stereochemistry to these epoxides on the basis of comparisons between the $^1$H n.m.r. spectra of *endo*-[4] and *exo*-5,6-epoxybicyclo[2.2.1]hept-2-ene [5] relative to bicyclo[2.2.1]hept-2-ene on the one hand and between epoxides (8) and (7) relative to the *endo*-adduct (14) and its *exo*-isomer ‡ on the other, afforded inconclusive results. Also it was particularly noteworthy that on epoxidation of quinones (6) and (10), the n.m.r. spectra showed a marked *increase* § in the amount of photolabile

* Synthetic work. † Crystallography.

‡ The spectrum measured for the crude product (14) obtained directly from the Diels–Alder reaction showed signals attributable to small quantities of the *exo*-isomer.

§ The epoxidation reactions are very clean, leading quantitatively to the products. Epoxidations of the quinones (5), (6), and (10) were carried out under identical conditions. Approximate *exo* : *endo* ratios were determined by n.m.r. integration.

epoxide formed, compared with that obtained by epoxidation of quinone (5). The proportions from typical reactions (see Table 1) are 43% [from (5)], 75% [from (6)], and 70% [from (10)]. Since approach of the reagent to the *exo*-face of quinone (5) must be more sterically crowded, compared to the *endo*-face, than in the case of quinones (6) and (10), the *exo* : *endo* ratios would be expected to be higher for the epoxides of (6) and (10). These results imply that the photolabile isomers are the *exo*-epoxides (3), (8), and (12), which has now been unambiguously demonstrated by an *X*-ray crystallographic determination of the bromo-epoxide, from the pair (11) and (12), which did not photorearrange in sunlight. This was shown to be *endo*-epoxide (11) (see below).

Mechanisms can be drawn to accommodate both the photochemical and alcohol-induced reactions. In the former case, a plausible intermediate (15) could rearrange *via* (16) to the product (4) as shown. If intermediate (15) does occur, one might expect a related intermediate (but with different stereochemistry) to arise from irradiation of the *endo*-epoxide (2), although, as mentioned earlier, sunlight irradiation left (2) essentially unchanged. However, brief irradiation of pure compound (2) under nitrogen with a 450-W high-pressure Hanovia mercury-vapour photoreactor using a Pyrex filter partly converted it into quinone (4).

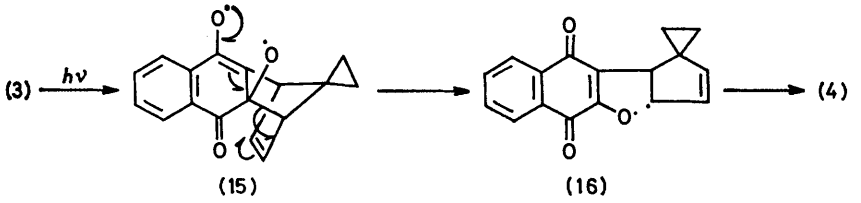
Finally, the quinones (5) and (6) were methylenated with dimethyloxosulphonium methylide in dimethyl sulphoxide [6] to afford the mixtures (17) and (18), and (19) and (20), respectively. These pairs of compounds showed no tendency to undergo photoisomerisation either in sunlight or in ultraviolet light. Aliphatic signals of the $^1$H n.m.r. spectra are recorded in Table 2. Stereochemical assignments could be made from changes in the *exo* : *endo* ratios and by comparison with data assembled in Table 1.

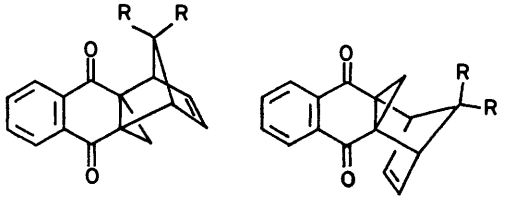
TABLE 1

Chemical shifts * of the aliphatic protons of the epoxides

| Compound | 2-H and 3-H (t, $J$ 2 Hz) | 1-H and 4-H(m) | Bridge or cyclopropyl H(m) | Yield (%) |
|---|---|---|---|---|
| (*a*) Photolabile epoxides | | | | |
| 2 or 3 | 3.34 | 6.86 | 9.20 | 43 |
| 7 or 8 | 3.38 | 6.38 | 8.26 | 75 |
| 11 or 12 | 3.40 | 6.38 | 8.29 | 70 |
| (*b*) Remaining epoxides | | | | |
| 2 or 3 | 3.80 | 6.70 | 9.48 | 57 |
| 7 or 8 | 3.82 | 6.22 | 7.83 | 25 |
| 11 or 12 | 3.84 | 6.23 | 7.83 | 30 |

* Spectra observed in $CDCl_3$ as 0.15M solutions.




(17) RR = $[CH_2]_2$ (18) RR = $[CH_2]_2$
(19) R = H (20) R = H

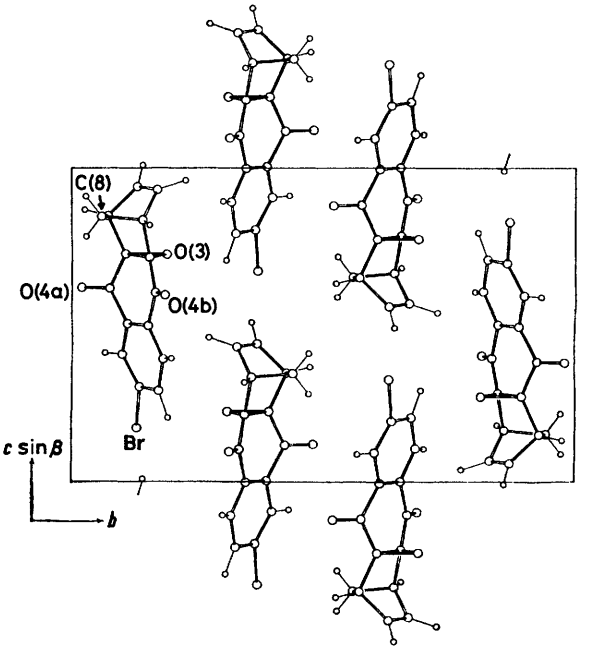



FIGURE 1 Unit cell contents projected down *a*

*Crystal Structure of the Bromo-epoxide* (11).—Within the molecular non-hydrogen skeleton, the observed geometry is as expected within the rather large limits of error insofar as interatomic distances and angles are concerned. Nevertheless, in addition to establishing

the overall stereochemistry, some features of interest emerge from a study of the interplanar angles of the molecular skeleton (see Table 3). It will be seen from Table 3 and Figure 3, which displays the angles between these planes, that these angles are quite variable and, notably, that the carbonyl groups of the quinonoid ring are not coplanar with the benzene ring, being buckled out of the ring in the opposite direction to the epoxide ring.

TABLE 2

Chemical shifts [a] of the aliphatic protons of the cyclopropanes (17)—(20)

| Compound | 2-H and 3-H (t, $J$ 2 Hz) | 1-H and 4-H(m) | 4a- and 9a-$CH_2$ (2 d, $J$ 6 Hz) | Cyclopropyl or 1,4-$CH_2$(m) | Yield (%) |
|---|---|---|---|---|---|
| (17) | 3.78 | 6.66 | 7.76 and 8.05 | 9.53 | 70 |
| (18) | 3.32 | 6.96 | 6.56 and 7.72 | 9.20 | 30 |
| (19) | 3.86 | 6.18 | 8.15 [b] | 8.20 | 35 |
| (20) | 3.42 | 6.44 | 7.29 and 7.76 | 8.62 | 65 |

[a] Spectra observed in $CDCl_3$ as 0.15M solutions. [b] Other doublet obscured.

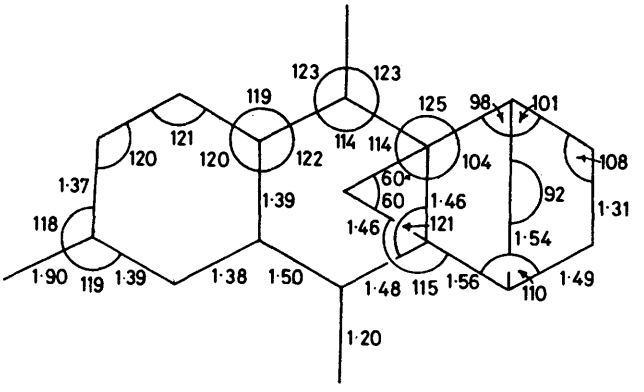



FIGURE 2 Mean molecular geometry of non-hydrogen atoms (bond lengths in Å, bond angles in degrees)

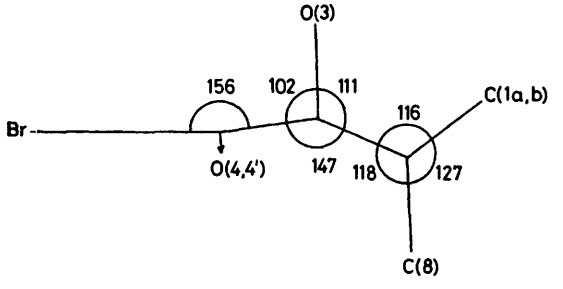



FIGURE 3 Interplanar angles within the non-hydrogen skeleton of the molecule (°)

## EXPERIMENTAL

I.r. spectra were measured for Nujol mulls and n.m.r. spectra for solutions in $CDCl_3$ with tetramethylsilane as internal reference. Chromatography was carried out using Merck Kieselgel (30—70 mesh). Light petroleum refers to the fraction of b.p. 60—80 °C.

1,4,4a,9a-*Tetrahydro*-endo-4a,9a-*epoxy*-1,4-*methano*-*anthraquinone*-11-*spirocyclopropane* (2) *and the* exo-*Isomer* (3).—(*a*) *From the adduct* (1). Sodium hydroxide (2M, 3 ml) was added to a stirred solution of the adduct (1) (2.00 g) in methanol (180 ml) at 35 °C. Stirring was continued at 35—40 °C for a further 2 h and then the reaction mixture was neutralised, poured into water, and extracted with chloroform. The organic layer yielded a yellow solid (1.95 g) which was fractionally crystallised to afford the *endo*-epoxide (2) as long white needles (1.00 g, 47%), m.p. 169—170 °C (ethanol) (Found: C, 77.1; H, 4.5. $C_{17}H_{12}O_3$ requires C, 77.3; H, 4.6%); $\lambda_{max.}$ 228, 258, and 298 nm (log ε 4.56, 3.60, and 3.33); $\nu_{max.}$ 1 691 and 1 598 $cm^{-1}$. The mother liquors were chromatographed [ethyl acetate–light petroleum (1 : 20)]. Earlier fractions afforded a mixture of (2) and (3) (0.82 g). These were followed by the *quinone* (4) (58 mg, 3%), identical with material described below.

(*b*) *From the quinone* (5). The quinone (5) (240 mg) was dissolved in ethanol (50 ml) and an excess of hydrogen peroxide (30%) and sodium carbonate in water (20 ml) was added. The mixture, which rapidly decolourised, was stirred for 5 min and then partitioned between water and methylene chloride. The organic layer afforded a white

TABLE 3

Least-squares planes, calculated relative to the right-handed orthogonal (Å) reference frame ($X,Y,Z$) ($X = ax + cz \cos\beta$, $Y = by$, $Z = cz \sin\beta$) [atom deviations (Å) in square parentheses]

(i) Br, C(4a), C(4b), C(5a), C(5b), C(6a), C(6b), C(7a), and C(7b)
$$-0.5023X + 0.8269Y + 0.2528Z = 2.335$$
Br, 0.10; C(4a), −0.02; C(4b), 0.09; C(5a), 0.00; C(5b), 0.02; C(6a), −0.05; C(6b), −0.04; C(7a), −0.03; C(7b), −0.07; C(3a), 0.49; C(3b), 0.60; O(4a) −0.52; O(4b), −0.21]

(ii) C(3a), C(3b), C(4a), and C(4b)
$$-0.5709X + 0.8062Y - 0.1553Z = -0.687$$
[C(3a), −0.02; C(3b), 0.03; C(4a), 0.01; C(4b), −0.01; O(4a), −0.43; O(4b), −0.36]

(iii) C(3a), C(3b), and O(3)
$$0.0924X + 0.0007Y + 0.9957Z = 8.408$$
[C(3a), 0.0; C(3b), 0.0; O, 0.0]

(iv) C(2a), C(2b), C(3a), and C(3b)
$$-0.5000X + 0.7654Y + 0.4053Z = 3.994$$
[C(2a), 0.01; C(2b), −0.01; C(3a), −0.02; C(3b), 0.02]

(v) C(2a), C(2b), and C(8)
$$0.0245X + 0.0930Y + 0.9954Z = 9.806$$
[C(2a), 0.0; C(2b), 0.0; C(8), 0.0]

(vi) C(1a), C(1b), C(2a), and C(2b)
$$-0.4692X + 0.6048Y - 0.6435Z = -6.302$$
[C(1a), 0.00; C(1b), 0.00; C(2a), 0.00; C(2b). 0.00]

The equations of the carbonyl planes C(4), O(4), C(3), and C(5) segments (a) and (b) [atom deviations (Å) in square parentheses]

(a) $$-0.8144X + 0.5770Y + 0.0622Z = 0.233$$
[C(4a), 0.03; O(4a), −0.01; C(3a), −0.01; C(5a), −0.01]

(b) $$-0.2890X + 0.9573Y + 0.0054Z = 1.891$$
[C(4b), −0.01; O(4b), 0.00; C(3b), 0.00; C(5b), 0.00]

The dihedrals with planes (i) and (ii) are (°)

| | |
|---|---|
| (a)—(i) 26 | (b)—(i) 20 |
| (a)—(ii) 23 | (b)—(ii) 21 |

crystalline mixture of the epoxides (2) (57%) and (3) (43%) (proportions determined approximately by n.m.r. integration) (255 mg). Successive recrystallisations from ethanol provided material identical with the *endo*-epoxide above.

1,4,4a,9a-*Tetrahydro*-endo-4a,9a-*epoxy*-1,4-*methanoanthraquinone* (7) *and the* exo-*Isomer* (8).—These were obtained quantitatively by treatment of the quinone (6) as above with hydrogen peroxide in aqueous sodium carbonate. Successive recrystallisations afforded the *exo*-epoxide, contaminated by *ca.* 10% of the *endo*-isomer (Found: C, 75.6; H, 4.5. $C_{15}H_{10}O_3$ requires C, 75.6; H, 4.2%).

6-*Bromo*-1,4,4a,9a-*tetrahydro*-1,4-*methanoanthraquinone*.—6-Bromonaphthoquinone [7] (4.40 g) was dissolved in benzene containing freshly distilled cyclopentadiene (4 ml), and the mixture was refluxed for 14 h. Removal of the solvent afforded the *product* (4.78 g, 85%), m.p. 106—107 °C (cyclohexane) (Found: C, 59.65; H, 3.65. $C_{15}H_{11}BrO_2$ requires C, 59.4; H, 3.6%); $\nu_{max.}$ 1 725 and 1 578 $cm^{-1}$; $\tau$ 1.83 (1 H, s, 5-H), 2.33 (2 H, s, 7- and 8-H), 4.00 (2 H, t, *J* 2 Hz, 2- and 3-H), 6.33 (2 H, m, 1- and 4-H), 6.53 (2 H, m, 4a- and 9a-H), and 8.43 (2 H, m, 11-H).

6-*Bromo*-1,4-*dihydro*-1,4-*methanoanthraquinone* (10).—The foregoing adduct (3.50 g) was dissolved in dry tetrahydrofuran (150 ml) and treated with potassium t-butoxide (0.5 g) under nitrogen for 3 min, after which the mixture was poured into water and neutralised with dilute hydrochloric acid. The chloroform extract afforded a tar, which was redissolved in benzene (200 ml) and stirred with silver(I) oxide for 5 h. The filtrate afforded an orange oil which was chromatographed [eluant ethyl acetate–light petroleum (1 : 10)]. This gave the *quinone* (10) (3.04 g, 87%), m.p. 143—143.5 °C (ethanol) (Found: C, 59.8; H, 2.95. $C_{15}H_9BrO_2$ requires C, 59.8; H, 3.0%); $\nu_{max.}$ 1 660 and 1 584 $cm^{-1}$; $\tau$ 1.80 (1 H, s, 5-H), 2.10 (2 H, s, 7- and 8-H), 3.07 (2 H, t, *J* 2 Hz, 2- and 3-H), 5.72 (2 H, m, 1- and 4-H), and 7.61 (2 H, m, 11-H).

6-*Bromo*-1,4,4a,9a-*tetrahydro*-endo-4a,9a-*epoxy*-1,4-*methanoanthraquinone* (11) *and the* exo-*Isomer* (12).—These were obtained quantitatively by treatment of the quinone (10) as above with hydrogen peroxide and aqueous sodium carbonate.

*General Procedure for the Sunlight Irradiation of the Epoxide Mixtures*.—The epoxide mixture was dissolved in dry benzene in a Pyrex flask, flushed with nitrogen, sealed, and irradiated in sunlight until all the *exo*-epoxide had rearranged. The solution was then evaporated and the residue chromatographed [eluant ethyl acetate–light petroleum (1 : 20)]. The *endo*-epoxide eluted first, followed by the quinone.

2,4a-*Dihydronaphtho*[2,3-b]*cyclopenta*[d]*furan*-5,10(4H)-*dione*-4-*spirocyclopropane* (4).—The epoxide mixture (115 mg) consisting of (2) (65 mg) and (3) (50 mg) was irradiated as above for 20 h. Chromatography afforded (2) (57 mg) followed by the *photoproduct* (43 mg, 86%), m.p. 204 °C (decomp.) (Found: C, 77.2; H, 4.6. $C_{17}H_{12}O_3$ requires C, 77.3; H, 4.6%); $\lambda_{max.}$ 252, 282, 327, and 393 nm (log $\varepsilon$ 4.39, 4.20, 3.45, and 3.07); $\nu_{max.}$ 1 683, 1 642, 1 613, and 1 592 $cm^{-1}$; $\tau$ 1.94 (2 H, m, 6- and 9-H), 2.33 (2 H, m, 7- and 8-H), 3.78 (1 H, dd, *J* 9 and 2.5 Hz, 3a-H), 4.10 (1 H, dd, *J* 2.5 and 5.5 Hz, 3-H), 4.38 (1 H, d, *J* 5.5 Hz, 2-H), 6.02 (1 H, d, *J* 9 Hz, 10b-H), and 8.7—9.6 (4 H, m, cyclopropyl).

2,4a-*Dihydronaphtho*[2,3-b]*cyclopenta*[d]*furan*-5,10(4H)-*dione* (9).—The epoxide mixture (155 mg) consisting of (7) (39 mg) and (8) (116 mg) was irradiated as above for 25 h, Chromatography afforded first epoxides (7) (28 mg, 72%) and (8) (37 mg, 32%) followed by photoproduct (9) (39 mg, 34%), m.p. 189—190 °C (Found: C, 75.6; H, 4.4. $C_{15}H_{10}O_3$ requires C, 75.6; H, 4.2%); $\lambda_{max.}$ 252, 286, 338, and 391 nm (log $\varepsilon$ 4.36, 4.08, 3.41, and 3.05); $\nu_{max.}$ 1 680, 1 649, 1 620, and 1 594 $cm^{-1}$; $\tau$ 1.98 (2 H, m, 6- and 9-H), 2.33 (2 H, m, 7- and 8-H), 3.7—4.2 (3 H, m, 2-, 3-, and 3a-H), 5.7—6.1 (1 H, m, 10b-H), and 7.0—7.3 (2 H, m, $CH_2$). Subsequent re-irradiation for 16 h of the epoxide recovered as above afforded (7) (24 mg, 60%), but (8) was entirely converted into quinone (9). The total yield of (9) was 53 mg, 46%.

7-(*or* 8)-*Bromo*-2,4a-*dihydronaphtho*[2,3-b]*cyclopenta*[d]-*furan*-5,10(4H)-*dione* (13).—The epoxide mixture (500 mg) consisting of (11) (150 mg) and (12) (350 mg) was irradiated as above for 16 h. The reaction mixture was chromatographed to separate epoxides (11) and (12) from the quinone (13). The epoxide mixture so obtained was twice more irradiated for periods of 16 h, each period of irradiation being followed by chromatography. This afforded epoxide (11) (100 mg, 67%) and quinone (13) (175 mg, 50%), m.p. 150 °C (decomp.) (ethanol) (Found: C, 56.75; H, 2.95. $C_{15}H_9BrO_3$ requires C, 56.8; H, 2.85%); $\nu_{max.}$ 1 678, 1 640, 1 620, and 1 579 $cm^{-1}$; $\tau$ 1.83 [1 H, m, 6-(or 9)-H], 2.0—2.3 [2 H, m, 8- and 9-(or 6- and 7-)-H], 3.7—4.1 (3 H, m, 2-, 3-, and 3a-H), 5.86 (1 H, m, 10b-H), 6.8—7.5 (2 H, m, $CH_2$).

*Sunlight Irradiation of* endo-*Epoxide* (2).—Pure *endo*-epoxide (2) (92 mg) was irradiated for 20 h as above. Chromatography afforded the *endo*-epoxide (2) (85 mg).

*Ultraviolet Irradiation of the* endo-*Epoxide* (2).—Pure *endo*-epoxide (2) (148 mg) was dissolved in benzene (500 ml) and irradiated through Pyrex for 25 min with a mercury-vapour photoreactor. Chromatography as above afforded starting material (2) (98 mg, 66%) and quinone (4) (49 mg, 33%).

1,4,4a,9a-*Tetrahydro*-endo-4a,9a-*methano*-1,4-*methanoanthraquinone*-11-*spirocyclopropane* (17) *and the* exo-*Isomer* (18).—Sodium hydride (0.58 g, 60% dispersion) was placed in a 3-necked flask, one neck of which was fitted with a septum. The sodium hydride was washed free of oil with light petroleum (b.p. 40—60 °C). Trimethyloxosulphonium iodide (0.265 g) was rapidly added, the system was flushed with nitrogen, and dry dimethyl sulphoxide (1.5 ml) was slowly added from a hypodermic syringe. After 20 min the quinone (5) (0.30 g) was slowly added in dry dimethyl sulphoxide (10 ml) through the syringe. The mixture was stirred for a further 15 min and then warmed on a water-bath for 1 h at 50—55 °C. The mixture was then cooled and partitioned between water and much ether. The organic layer yielded the products (17) and (18) quantitatively, in the ratio (n.m.r.) 70 : 30. The mixture could be recrystallised from ethanol (Found: C, 82.1; H, 5.1. $C_{18}H_{14}O_2$ requires C, 82.3; H, 5.3%).

1,4,4a,9a-*Tetrahydro*-endo-4a,9a-*methano*-1,4-*methanoanthraquinone* (19) *and the* exo-*Isomer* (20).—When the quinone (6) (0.25 g) was treated as in the foregoing reaction, the products isolated (0.26 g, 98%) were (19) (35%) and (20) (65%). The mixture was recrystallised from ethanol (Found: C, 81.3; H, 5.0. $C_{16}H_{12}O_2$ requires C, 81.3; H, 5.1%).

*Crystal Structure Determination of Compound* (11).—Material isolated by chromatography from the photochemical reaction to convert compound (12) to the quinone (13) was recrystallised from ethanol. A needle 0.40 ×

TABLE 4

Non-hydrogen fractional cell parameters ($\times 10^4$)

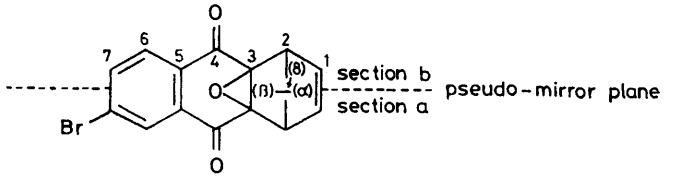
| | Section a | | | Section b | | |
|---|---|---|---|---|---|---|
| Atom | $x$ | $y$ | $z$ | $x$ | $y$ | $z$ |
| C(1) | 4 843(40) | 1 306(13) | 9 414(16) | 6 683(38) | 1 699(12) | 9 305(18) |
| C(2) | 4 842(39) | 727(11) | 8 482(16) | 7 921(31) | 1 414(14) | 8 341(19) |
| C(3) | 4 390(28) | 1 070(10) | 7 256(15) | 6 357(31) | 1 548(9) | 7 161(14) |
| O(3) | 4 212(19) | 1 889(7) | 7 263(9) | | | |
| C(4) | 3 233(13) | 748(11) | 6 174(14) | 7 360(32) | 1 667(9) | 6 035(15) |
| O(4) | 2 111(26) | 193(8) | 6 199(11) | 9 275(19) | 1 861(7) | 5 967(9) |
| C(5) | 3 737(29) | 1 122(10) | 5 048(12) | 5 712(29) | 1 535(9) | 4 998(14) |
| C(6) | 2 178(29) | 1 013(9) | 4 064(16) | 6 091(26) | 1 818(10) | 3 935(15) |
| C(7) | 2 600(31) | 1 350(10) | 3 031(15) | 4 570(29) | 1 736(10) | 2 923(14) |
| (C8) | 7 467(41) | 594(12) | 8 469(20) | | | |
| Br | 0 365(3) | 1 298(1) | 1 721(2) | | | |

0.16 × 0.07 mm was used for the crystallographic work. Unit-cell dimensions were obtained from a least-squares fit of the angular parameters of 15 reflections with 2θ *ca.* 15° centred in the counter aperture of a Syntex $P\bar{1}$ four-circle diffractometer; a unique data set was then gathered in the range $2\theta < 40°$ (the limit being imposed by the small size and quality of the available material), yielding 1 135 independent reflections, 669 of which [with $I > 2\sigma(I)$] were considered ' observed ' and used in the structure solution and refinement after correction for absorption; the temperature was 295(1) K.

*Crystal data.* $C_{15}H_9BrO_3$, $M = 317$. Monoclinic, space group $P2_1/n$ (variant of $C_{2h}^5$, no. 14), $a = 5.870(5)$, $b = 18.13(1)$, $c = 11.475(6)$ Å, $\beta = 95.84(6)°$, $U = 1\ 215(1)$ Å$^3$, $D_m = 1.73(1)$ g cm$^{-3}$, $Z = 4$, $D_c = 1.73$ g cm$^{-3}$, $F(000) = 632$, monochromatic Mo-$K_\alpha$ radiation, $\lambda = 0.710\ 69$ Å, $\mu = 32.9$ cm$^{-1}$. Neutral atom scattering factors, those for the non-hydrogen atoms being corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$).[8-10]

The structure was solved by the heavy-atom method and refined by full-matrix least squares; all non-hydrogen atoms were refined with anisotropic thermal tensors, $U_{ij}$ for the non-hydrogen atoms; isotropic thermal parameters $U$ were constrained at $U = \langle 0.01 + U_{ii} \rangle$ Å, $U_{ii}$ pertaining to the associated carbon. In spite of the rather over-parametrized nature of the refinement (200 variables, 669 observations), refinement proceeded smoothly and apparently meaningfully to convergence, no parameter shift in the final least squares cycle exceeding 0.2σ. Final $R\{= (\Sigma||F_o| - |F_c||)/\Sigma|F_o|\}$ was 0.062, $R'\{= [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\} = 0.057$. In the weighting scheme, of the form $w = [\sigma^2(F_o) + n \times 10^{-4}(F_o)^2]^{-1}$, the optimum $n$ was found to be 3.

Computation was carried out using a local adaptation of the ' *X*-RAY '76 ' program system [11] implemented on a CYBER 73 computer. Structure amplitudes, thermal parameters, and hydrogen atom parameters are given in Supplementary Publication No. SUP 22376 (18 pp.).* Results are given in Tables 4 and 5. For convenience, because of




the pseudo-mirror plane in the molecular skeleton, atom numbering is as above, the two halves of the molecule generated by the plane being denoted ' a ' and ' b '. Oxygen and hydrogen atoms are labelled according to the parent carbon, suffixed α, β for C(8) Br lies in section a.

* For details, see Notice to Authors No 7, *J.C.S. Perkin I*, 1978, Index issue.

TABLE 5

Molecular geometry; values for section b follow those for section a. Primes denote atoms in the other half of the molecule

| Bond lengths/Å | | Bond angles/° | |
|---|---|---|---|
| C(1)–C(1′) | 1.31(3) | C(1′)–C(1)–C(2) | 105(2), 111(2) |
| C(1)–C(2) | 1.50(3), 1.48(3) | C(1)–C(2)–C(3) | 111(2), 108(2) |
| C(2)–C(3) | 1.54(2), 1.58(3) | C(1)–C(2)–C(8) | 101(2), 100(2) |
| | | C(3)–C(2)–C(8) | 98(2), 98(2) |
| C(2)–C(8) | 1.56(3), 1.52(3) | C(2)–C(8)–C(2′) | 92(2) |
| C(3)–C(4) | 1.47(2), 1.49(3) | C(2)–C(3)–C(3′) | 104(1), 104(1) |
| C(3)–O(8) | 1.49(2), 1.42(2) | C(2)–C(3)–O(8) | 114(1), 116(1) |
| C(3)–C(3′) | 1.46(2) | C(2)–C(3)–C(4) | 129(2), 121(2) |
| C(4)–O(4) | 1.20(2), 1.19(2) | O(8)–C(3)–C(3′) | 58(1), 62(1) |
| C(4)–C(5) | 1.52(2), 1.48(2) | O(8)–C(3)–C(4) | 111(1), 116(1) |
| C(5)–C(5′) | 1.39(2) | C(3′)–C(3)–C(4) | 118(2), 123(1) |
| C(5)–C(6) | 1.39(2), 1.36(2) | C(3)–O(3)–C(3′) | 60(1) |
| C(6)–C(7) | 1.38(3), 1.40(2) | C(3)–C(4)–O(4) | 121(2), 124(2) |
| C(7)–C(7′) | 1.37(3) | C(3)–C(4)–C(5) | 115(2), 113(2) |
| C(7)–Br | 1.90(2) | O(4)–C(4)–C(5) | 123(1), 123(2) |
| | | C(4)–C(5)–C(5′) | 121(1), 122(1) |
| | | C(4)–C(5)–C(6) | 117(2), 121(2) |
| | | C(5′)–C(5)–C(6) | 122(1), 117(1) |
| | | C(5)–C(6)–C(7) | 118(2), 124(2) |
| | | C(6)–C(7)–C(7′) | 122(1), 117(2) |
| | | C(6)–C(7)–Br | 119(1) |
| | | C(7′)–C(7)–Br | 118(1) |

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