The Di-π-methane Rearrangements of 1,4-Dihydro-1,4-methano- and -ethanonaphthalene-5,8-diols

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Direct photolysis of 1,4-dihydro-1,4-methanonaphthalene-5,8-diol (1a) gave tetracyclo[5.4.0.0^{2,4}.0^{3,6}]undeca-1(7),8,10-triene-8,11-diol (2a), the structure of which was established by spectral data and conversion into the known diacetate (2b). Photolysis of the 1,4-ethano-derivative (1g) gave tetracyclo[6.4.0.0^{2,4}.0^{3,7}]dodeca-1(8),9,11-triene-9,12-diol (2d), identified from spectral data. An X-ray crystallographic study of its diacetate (2e) showed that the crystals are orthorhombic, space group *Pnma*, $a = 8.37(2)$, $b = 18.60(3)$, $c = 9.49(2)$ Å, $Z = 4$, with 50% occupation of equivalent positions by enantiomer pairs to produce a disordered structure. The structure was solved by direct methods and atomic positions and thermal parameters were refined by full-matrix least-squares calculations and Fourier methods. Studies with the 2,3,6,7-tetradeuterio-derivatives of (1a) and (1g) showed that the rearrangements are of the di-π-methane–vinylcyclopropane type.

FOLLOWING our work [1,2] on the photorearrangement of thebainehydroquinone, we have studied the photo-reactions of the bridged bicyclic hydroquinones (1a and g) as models for thebainehydroquinone. As discussed below, these compounds behave similarly to thebaine-hydroquinone in undergoing the di-π-methane-to-vinyl-cyclopropane photorearrangement.[3] The di-π-methane rearrangement proceeds through a singlet excited state in acyclic and certain monocyclic molecules.[3] In these systems free rotation about the unconstrained π-bonds can bring about efficient deactivation of their triplet states. By contrast, cyclic compounds, in which the molecular structure prevents free rotation about the excited π-bonds, usually only undergo the di-π-methane rearrangement in the presence of sensitizers, and so are believed to rearrange through the triplet state. On direct irradiation these compounds normally either do not react, or undergo a different reaction.[3,4] However there are cyclic compounds with constrained bonds which undergo the rearrangement on direct irradiation,[5] and the reactions we discuss here [1] and that of thebaine-hydroquinone [2] are of this type.

for the aliphatic portions of the n.m.r. spectrum of (2a) (Figure 1) are given in Table 1. The high-field signal
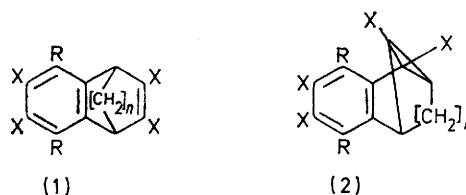
(1)

a; R = OH, X = H, n = 1
b; R = OAc, X = H, n = 1
c; R = OH, X = D, n = 1
d; R = ThpO, X = H, n = 1
e; R = ThpO, X = D, n = 1
f; R = X = H, n = 1
g; R = OH, X = H, n = 2
h; R = OH, X = D, n = 2
i; R = ThpO, X = H, n = 2
j; R = H, X = D, n = 1
k; R = OMe, X = H, n = 1

(2)

a; R = OH, X = H, n = 1
b; R = OAc, X = H, n = 1
c; R = OH, X = D, n = 1
d; R = OH, X = H, n = 2
e; R = OAc, X = H, n = 2
f; R = OH, X = D, n = 2
g; R = OAc, X = D, n = 2
h; R = X = H, n = 1
i; R = H, X = D, n = 1
j; R = OMe, X = H, n = 1

(F) is assigned to the *endo*-proton, H-2.[4a,5a,6] Irradiation at the frequency of this signal causes simplification of signals B and C. Irradiation at the frequency of signal C transforms signal F to a doublet with J 2.7 Hz. Signal C is assigned to H-3 because it is the only proton which would have a large coupling constant (8.6 Hz) with H-2. Small couplings (0.3 and 0.0 Hz) are assigned to $J_{1,2}$ and $J_{2,4}$ because the torsion angles between those protons and H-2

spectrum plotted by using these parameters agreed closely with that shown in Figure 1.†

Direct irradiation of the ethano-compound (1g) under conditions similar to those used for (1a) gave a 48% yield of tetracyclo[6.4.0.0^{2,4}.0^{3,7}]dodeca-1(8),9,11-triene-9,12-diol (2d). The identification of (2d) was based originally on its spectral properties and those of its diacetate (2e), and on analogy with the transformation (1a) ——▶ (2a).
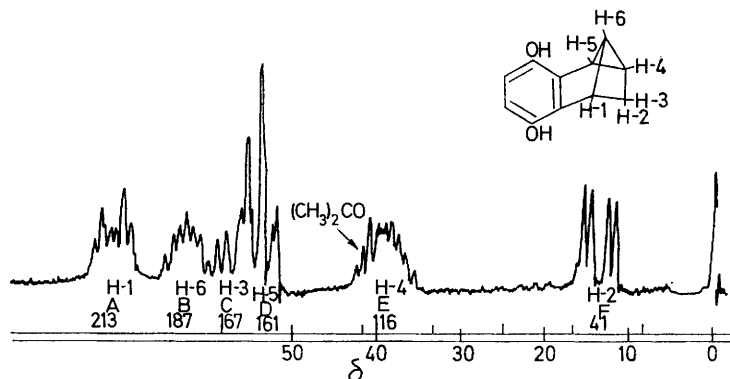

FIGURE 1 N.m.r. spectrum of alicyclic protons in the tetracyclic diol (2a)

are very close to 90°.[7] The 2.7 Hz splitting of signal F is assigned to long-range coupling between H-2 and -6,[8] and so B is the signal for H-6. Irradiation at the frequency of signal E changes signals A—D. Signal E therefore is assigned to H-4 because its position in the bridged ring system suggests that it will couple with all the other protons except H-2. Since H-1 is both a benzylic and a bridgehead proton and is not attached to a cyclopropane ring carbon

The high-field portion of the ^{1}H n.m.r. spectrum of (2d) shows some resemblance to that of benzosemibullvalene (3).[4d] Irradiation at the frequency of the signal at δ 3.57 causes the quartet at δ 2.61 to collapse to a triplet, J 5.5 Hz, and changes the signal at δ 1.74. Simultaneous irradiation at the frequencies of the signals at δ 2.61 and 2.39 causes the triplet at 3.57 to collapse to a doublet, J 4 Hz, and some simplification of the multiplet at 1.74. In neither of these

TABLE 1

Calculated n.m.r. chemical shifts (at 60 MHz, in Hz downfield from Me$_4$Si) and coupling constants (Hz) of alicyclic protons in (2a)

H-1	213.3	H-2	40.9	H-3	167.5	H-4	116.0	H-5	161.5	H-6	187.3
$J_{1,2}$	0.3	$J_{2,3}$	−8.6	$J_{3,4}$	3.4	$J_{4,5}$	5.4	$J_{5,6}$	5.0		
$J_{1,3}$	7.2	$J_{2,4}$	0.0	$J_{3,5}$	0.0	$J_{4,6}$	4.8				
$J_{1,4}$	2.4	$J_{2,5}$	0.0	$J_{3,6}$	0.0						
$J_{1,5}$	0.0	$J_{2,6}$	2.7								
$J_{1,6}$	2.9										

atom, its chemical shift is expected to be the largest of all those of the alicyclic protons; it is thus assigned signal A. Irradiation at the frequency of signal A causes changes in signals B, C, and E but not D or F. Thus signal D is assigned to H-5. Signal D is essentially a triplet, reflecting the expected similar coupling between H-5 and its neighbours H-6 and -4. The coupling constants and shifts reported in Table 1 were calculated by using the computer program devised by Castellano and Bothner-By;[9] the

decoupling experiments was any change detected in the signal at δ 1.15. When the frequency of the signal at δ 1.15 is irradiated, the signal at 1.74 alters considerably, but no change in the signals at δ 3.57, 2.61, and 2.39 is detected.

On the basis of these decoupling experiments, which parallel those performed on (3),[4d] we assign the n.m.r. signals for (2d), in a way similar to those for (3), as follows: ‡ δ 3.51, H-1; δ 2.61 (q), H-8; and δ 2.39 (t), H-7. If we assume that one of the *endo*-protons in compound (2d) is shielded by the benzene ring current as in compound (2a), the signal at δ 1.15 may be assigned to either H-2 or -4.

† The alicyclic portion of the n.m.r. spectrum of (2h) is similar to that of (2a). Edman's [4a,c] revised assignments of peaks correspond to ours for (2a) except that he reverses the protons 5 and 6 (signals B and D). We think our assignments account better for the magnitudes of the coupling constants and agree better with Zimmerman's [4d] discussion of the spectrum of (3). However our disagreement with Edman does not affect the results of our or his studies with deuteriated compounds.

‡ Numbering scheme analogous to that for (2a) (Figure 1), with the extra CH$_2$ group containing H-4 and -5; H-5 and -6 in (2a) correspond to H-7 and -8 in (2d)

[6] P. R. Story, *J. Amer. Chem. Soc.*, 1961, **83**, 3347.
[7] N. S. Bhacca and D. H. Williams, 'Applications of N.M.R. Spectroscopy in Organic Chemistry,' Holden-Day, San Francisco, 1964, pp. 49—52.
[8] J. Meinwald and A. Lewis, *J. Amer. Chem. Soc.*, 1961, **83**, 2769.
[9] S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, 1964, **41**, 3862.

The other alicyclic proton signals are located in the complex multiplet at δ 1.74.

The assignment of signals for H-1, -7, and -8 has been confirmed by a study with the shift reagent Eu(fod)₃. A model of structure (2d) suggests that the distances of hydrogen atoms from a shift reagent co-ordinated to the phenolic groups are in the order H-7 < H-1 < H-8. At a 0.5 molar ratio of Eu(fod)₃ to diol, the shifts (Table 2) of the

TABLE 2

Relation of chemical shifts to molar ratio between shift reagent and the diol (2d)

Molar ratio of Eu(fod)₃ to diol	Chemical shift (Hz) at 100 HMz		
	H-1	H-7	H-8
0	346	221	245
0.13 : 1	367	241—261	
0.24 : 1	392	258—282	
0.50 : 1	452	343	296
Δν (0.50—0)	106	122	51

signals we assigned to H-7, -1, and -8 are 122, 106, and 52 Hz, as expected.

The ¹³C n.m.r. spectrum and the results of an X-ray crystallographic study of the diacetate (2e) are consistent with the assigned structure. However assignment of ¹³C peaks to the cyclopropane carbon atoms not adjacent to the benzene ring is only possible after examining the spectrum of the deuteriated compound (2g) (see below).

Mechanistic Studies.—To help determine the pathway of the reaction of compound (1a) we irradiated the deuteriated compound (1c) [made by treating the tetrahydropyranyl ether (1d) with lithium cyclohexyl[²H]amide followed by acidic work-up of the deuteriated ether (1e)]. The ¹H n.m.r. spectrum of the product did not contain signals D and B (Figure 1); hence it has structure (2c), with deuterium substituted for H-5 and -6 of (2a).

The deuteriated compound (1h) was prepared by way of the tetrahydropyranyl ether (1i). Irradiation of (1h) gave (2f), the positions of the deuterium atoms being determined by ¹H n.m.r. comparison with (2d); the peaks corresponding to H-7 and -8 were reduced in intensity.

The photoreaction of compound (1a) was inhibited by a Pyrex filter but not by a Corex one. Addition of aceto-phenone or xanthen-9-one did not increase the yield or shorten the reaction time. The reaction was not quenched by oxygen or by isoprene (except in high concentrations). Similarly, when (1g) was irradiated through Pyrex in the presence of xanthen-9-one no reaction took place, and the presence of xanthen-9-one did not increase the yield of product when the irradiation was carried out with unfiltered light.

The fluorescence spectrum of compound (1a) (λ_max. 341 nm) is similar to that of hydroquinone (λ_max. 327 nm). The phosphorescence spectra of (1a), (1g), and hydroquinone are also similar to each other; in an ethanol glass they show a broad emission from 310 to 530 nm with maximum at 430 (1a and g) or 410 nm (hydroquinone). However the emission from (1g) is much more intense than that from (1a) and less intense than that from hydroquinone.

DISCUSSION

Structure of the Tetracyclic Diacetate (2e).—The atom numbering scheme employed and the packing of mole-

cules in the crystal as viewed along the c axis are shown in Figure 2. Interatomic distances and angles are in the Supplementary Publication.

Whereas X-ray diffraction studies on crystals having an ordered molecular arrangement lead to unambiguous identification of the atomic positions and hence to a unique structure, the situation is more complicated when structural disorder occurs as in the present investigation.
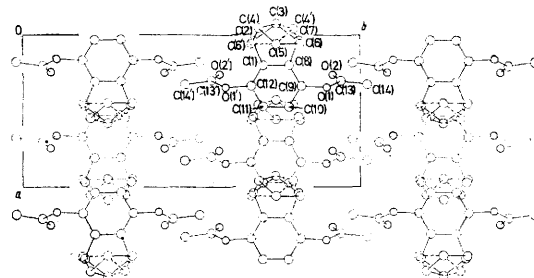

FIGURE 2 Atom numbering scheme and packing of diacetate (2e) molecules in the crystal, viewed in projection along the c axis; atoms C(4), C(6), C(4'), and C(6') have 50% occupancy

However, even with disordered structures, evaluation of all possible interatomic distances and valency angles may still lead to a unique conclusion in conjunction with spectral data. In the present study the electron density distribution and derived atomic positions are consistent with structure (2e). Unfortunately, owing to the presence of the structural disorder, it was not possible to obtain molecular dimensions of the desired accuracy to reveal any departures of the bond lengths and valency angles from their normal values. Means of the various bond types are in accord with expected values:[10] $C(sp^3)-C(sp^3)$ 1.55, $C(sp^3)-C(sp^2)$ 1.50, $C(ar)-C(ar)$ 1.40, $C(sp^2)-O$ 1.40, C=O 1.18 Å.

The equation of the least-squares plane through the acetate group atoms is $0.9423X - 0.0304Y - 0.3333Z - 0.8089 = 0$, where X, Y, and Z are in Å, and the small individual atom deviations [C(9) 0.01, O(1) −0.01, C(13) −0.03, O(2) 0.01, C(14) 0.02 Å] imply that they are coplanar as expected. For the phenyl ring atoms the least-squares plane has the equation $-0.3154X - 0.09490Z + 4.6719 = 0$, and the departures of the atoms from the plane [C(9) −0.04, C(10) 0.02, C(8) 0.02, O(1) −0.18 Å] indicate that there is a significant out-of-plane displacement of the oxygen atom substituent, presumably to relieve non-bonded interactions between the acetate carbonyl and the phenyl π-electrons. The torsion angle between the acetate group and phenyl ring plane is 89°.

There are no abnormally short intermolecular separations in the crystal; all exceed 3.53 Å and correspond to normal van der Waals interactions.

Mechanisms of the Rearrangements.—The phototransformations (1a) ⟶ (2a) and (1g) ⟶ (2d) are examples of di-π-methane-to-vinylcyclopropane rearrangements. The conversion of the deuteriated compounds (1c and h)

¹⁰ *Chem. Soc. Special Publ.*, No. 11, 1958; No. 18, 1965.

into (2c and f) show that in both reactions the C(1)–C(8a) bond is broken and a new one is formed between C(1) and C(3). This eliminates the possibility that the conversion (1a) ⟶ (2b) involves a [1,3] sigmatropic shift [see (4)].[11] A similar sigmatropic shift could not account for the conversion (1g) ⟶ (2d). The results, however, do not distinguish between the general di-π-methane mechanism [3] and a route involving a carbene,[12] which has been established for the reaction of triptycene,[5f] but not for dimethoxytriptycene.[5g]

The products (2a and d) are analogous to compounds (2b and h) that Edman [4a] obtained from (1b and f). Further, Edman reported [4b] that (1j) is transformed into (2i), and so his reaction involves similar bonds breaking and forming. However there is a significant difference between our results and his. As is usual for di-π-methane transformations of cyclic compounds with constrained π-bonds, Edman's reactions only took place in the presence of a sensitizer and he concluded that the reactions went through the triplet state. By contrast our reactions are unsensitized, and there is no agreement among authors about the nature of the photochemical intermediate in the unsensitized reactions. The T^1 state has been eliminated for some reactions; [5c,j] and the T^2 state was suggested for one of these reactions; [5j] the singlet state [5e] and T^1 [5i,m,n] states are also favoured for other reactions.

Our reaction (1a) ⟶ (2a) is not quenched by oxygen nor, except in high concentration, by isoprene. Phosphorescence is shown by (1a and g) and the intensities are less than that shown by hydroquinone. The lifetimes of the phosphoresences of (1a), (1g), and hydroquinone range from 1.7 to 3.5 s. These data, especially the phosphoresence shown by (1a and g) (*cf.* refs. 5c and 5i), suggest that our reactions, in contrast to the unsensitized rearrangement (1k) ⟶ (2j),[5i] go through the singlet state.

EXPERIMENTAL

Unless otherwise stated u.v. spectra were determined for solutions in 95% ethanol, i.r. spectra for KBr pellets, and ^{1}H n.m.r. spectra for solutions in [^{2}H$_6$]acetone (Varian A-60, A-60D, and XL100 spectrometers; decoupling studies were carried out with Varian A-60D and T-60 spectrometers). ^{13}C N.m.r. spectra were recorded with a Varian XL-100 instrument (with Fourier transform equipment). Emission spectra were determined with a Hitachi MPF-2A spectrometer with a phosphorescence attachment. Mass spectra were obtained with a Hitachi RMU-6D spectrometer operated at 70 eV. Irradiations were performed under nitrogen with Hanovia medium-pressure quartz mercury vapour lamps [608A-36 (100 W) and 679A-36 (450 W)], operated inside standard quartz immersion wells (Hanovia). Phosphorescence emissions were determined for solutions in ethanol or ether at 77 K, and lifetimes were measured with an oscilloscope.

1,4-Dihydro-1,4-methanonaphthalene-5,8-diyl Diacetate (1b).[13]—The diacetate (1b), obtained from 1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione, crystallized from ethanol in needles, m.p. 103—106° (lit.,[13] 106—106.5°), $\nu_{max.}$ 1 750, 1 640, and 1 600 cm^{-1}; $\lambda_{max.}$ (Et$_2$O) 266 nm (ϵ 300); δ (CDCl$_3$) 6.74 (2 H, m, vinylic), 6.58 (2 H, s, aromatic), 3.86 (2 H, m, bridgehead), 2.25 (6 H, s, Me), and 2.18 (2 H, m, bridge).

1,4-Dihydro-1,4-methanonaphthalene-5,8-diol (1a).[13]—The diol (1a), obtained from the diacetate (1b) by reduction with lithium aluminium hydride,[13] crystallized from toluene as plates, m.p. 144—146° (lit.,[13] 144—144.5°); $\nu_{max.}$ 3 700—3 100, 1 625, and 1 600 cm^{-1}; $\lambda_{max.}$ 299 nm (ϵ 3 480); $\lambda_{max.}$ (Et$_2$O) 303 nm (ϵ 3 700); δ 7.76 (2 H, s, OH), 6.78 (2 H, m, vinylic), 6.45 (2 H, s, aromatic), 4.20 (2 H, m, bridgehead), and 2.11 (2 H, m, bridge); fluorescence $\lambda_{max.}$ (in Et$_2$O excited at 314 nm) 341 nm; phosphorescence max. (EtOH) 436 nm (emission from 360 to 540 nm), τ_p 3.5 s, $\lambda_{max.}$ (ether) 412 nm.

Irradiation of the Diol (1a).—A stirred solution of the diol (1a) (3.58 g) in ether (2 150 ml) was irradiated for 2 h with the 450 W lamp. Evaporation under reduced pressure left an oily residue which on crystallization (charcoal) from chloroform yielded *tetracyclo*[5.4.0.0^{2,4}.0^{3,6}]*undeca*-1(7),8,10-*triene*-8,11-*diol* (2a) (1.48 g), prisms, m.p. 167—169°; $\nu_{max.}$ 3 650—3 100, 1 630, and 1 590 cm^{-1}; $\lambda_{max.}$ 295 nm (ϵ 3 400); δ 7.48 (2 H, s, OH), 6.49 (2 H, AB, aromatic), 3.55 (1 H, m), 3.10 (1 H, m), 2.77 (1 H, m), 2.70 (1 H, t, J 5 Hz), 1.90 (1 H, m), and 0.68 (1 H, m).

These conditions gave the best yield of photoproduct. Irradiation in 95% ethanol or ethyl acetate gave intractable products. Addition of acetophenone or xanthen-9-one as sensitizer did not increase the yield or shorten the time of reaction. Use of a Pyrex filter severely inhibited the reaction; use of Corex did not.

Irradiation of two samples of (1a), one of which had been degassed and the other not, through a Corex filter in a merry-go-round apparatus gave similar amounts of product (as determined from n.m.r. spectra). In similar irradiations of degassed solutions of (1a) (5.7 × 10^{-2}M) to which isoprene had been added in various amounts, the decrease in the amount of product (2a) only became appreciable at 0.5M-isoprene.

Tetracyclo[5.4.0.0^{2,4}.0^{3,6}]*undeca*-1(7),8,10-*triene*-8,11-*diyl Diacetate* (2b).—The diacetate (2b) [prepared by heating the diol (2a) with NaOAc–Ac$_2$O for 5 min on a steam-bath] crystallized from ethanol as needles, m.p. 153—156° (lit.,[4a] 160—160.5°); $\nu_{max.}$ 1 630 and 1 590 cm^{-1}; $\lambda_{max.}$ 265 nm (ϵ 275); δ (CDCl$_3$) 6.80 (2 H, AB, aromatic), 3.22 (2 H, m), 2.78 (1 H, m), 2.45 (1 H, t, J 5 Hz), 2.27 (3 H, s, Ac), 2.19 (3 H, s, Ac), 2.00 (1 H, m), and 0.81 (1 H, m). The i.r. and n.m.r. spectra were identical with those of an authentic sample obtained by sensitized irradiation of (1b).[4a]

Bistetrahydropyranyl Ether (1d) *of* 1,4-*Dihydro*-1,4-*methanonaphthalene*-5,8-*diol* (1d).—The diol (1a) (10 g) was added slowly to a stirred solution of concentrated hydrochloric acid (1 drop) in dihydropyran (10.6 g), and the mixture was stirred at 0 °C for 20 min. Chloroform (70 ml) was added and the solution was washed with aqueous sodium hydroxide (10%; 2 × 25 ml) and water (×2), dried (Na$_2$SO$_4$), and evaporated under reduced pressure. The residual oil was dissolved in cyclohexane (10 ml), light

[11] R. B. Woodward and R. Hoffmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 781.

[12] J. Ipaktschi, *Chem. Ber.*, 1972, **105**, 1989.

[13] J. Meinwald and G. A. Wiley, *J. Amer. Chem. Soc.*, 1958, **80**, 3667.

petroleum (50 ml) was added, and the solution was cooled and scratched to give the tetrahydropyranyl ether (1d) (8.33 g, 42%) as prisms, m.p. 92—94°; $\nu_{max.}$ 1 610 and 1 560 cm^{-1}; δ (CDCl$_3$) 6.79 (2 H, m, vinylic), 6.64 (2 H, s, aromatic), 5.22 (2 H, m, O·CH·O), 4.16 (2 H, m, bridgehead), 4.07—3.33 (4 H, m, O·CH$_2$), 2.18 (2 H, m, bridge), and 2.00—1.45 (12 H, m, pyran ring).

1,4-*Dihydro*-[2,3,6,7-^{2}H$_4$]-1,4-*methanonaphthalene*-5,8-*diol* (1c).—A solution of n-butyl-lithium in hexane (15 ml; 1.6M) was added, under nitrogen, to cyclohexyl[^{2}H$_2$]amine [14] (25 ml). The solution was stirred for 15 min and then a solution of the ether (1d) (5.01 g) in cyclohexyl[^{2}H$_2$]amine (35 ml) was added slowly. The mixture was stirred under nitrogen at 80 °C for ca. 80 h with further addition of the n-butyl-lithium solution (7 ml) after 23 and 44 h. The cooled mixture was quenched with D$_2$O (7 ml), and poured into hydrochloric acid (250 ml; 10%), thus hydrolysing the ether (1e). The mixture was extracted with ether (500 ml) and the extract was washed with hydrochloric acid (250 ml; 10%), then water, dried (Na$_2$SO$_4$), and evaporated under reduced pressure, leaving a brown oil. A solution of the oil in hot chloroform was cooled, yielding the diol (1c) (0.632 g, 25%). Analysis by n.m.r. showed 74% replacement by deuterium in the vinylic positions.

Irradiation of the [^{2}H$_4$]*Diol* (1c).—A solution of the diol (1c) (400 mg) in ether (180 ml) was irradiated for 1 h with the 450 W lamp. Evaporation followed by work-up as described for the non-deuteriated compound (2a) afforded compound (2c) (150 mg) as off-white crystals; δ 7.4br (2 H, s, OH), 3.53 (1 H, dd), 2.75 (1 H, td), 1.90 (1 H, m), and 0.65 (1 H, d, *J* 8.5 Hz).

1,4-*Dihydro*-1,4-*ethanonaphthalene*-5,8-*diol* (1g).—The diol (1g), prepared [15] from 1,4,4a,8a-tetrahydro-1,4-ethano-naphthalene-5,8-dione, crystallized from toluene in needles, m.p. 180—183° (lit.,[15] 178°); $\nu_{max.}$ 3 600—3 200, 1 645, and 1 600 cm^{-1}; $\lambda_{max.}$ 293 nm (ε 3 500); δ 7.63 (2 H, s, OH), 6.38 (4 H, m, aromatic and vinylic), 4.29 (2 H, m, bridgehead), and 1.30 (4 H, m, bridge); *m/e* 188 (25%, *M*$^+$), 160 (100), 132 (7), 105 (10), 103 (10), and 77 (15); *m** 136 (188 ⟶ 160) and 109 (160 ⟶ 132); phosphorescence $\lambda_{max.}$ (EtOH) 428 nm (emission from 360 to 550 nm), τ$_p$ 1.7 s, $\lambda_{max.}$ (ether) 408 nm, τ$_p$ 2.2 s.

Irradiation of the Diol (1g).—A stirred solution of the diol (1g) (0.3 g) in ether (175 ml) was irradiated for 13 min with the 450 W lamp. The solvent was removed under reduced pressure, and the oily residue, after trituration with light petroleum, crystallized from chloroform to give tetracyclo-[6.4.0.0^{2,4}.0^{3,7}]dodeca-1(8),9,11-triene-9,12-diol (2d), as needles, m.p. 147—149° (decomp.); $\nu_{max.}$ 3 700—3 200 and 1 610 cm^{-1}; $\lambda_{max.}$ 293 nm (ε 2 280); δ 7.33 (1 H, s, OH), 7.20 (1 H, s, OH), 6.48 (2 H, AB, aromatic), 3.70 (1 H, t, *J* 5 Hz), 2.58 (2 H, m), 1.86 (4 H, m), and 1.23 (1 H, m); δ (100 MHz) 7.22 (1 H, s, OH), 7.10 (1 H, s, OH), 6.31 (2 H, AB, aromatic), 3.57 (1 H, t, *J* 5 Hz), 2.61 (1 H, dd, *J* 13 and 5.5 Hz), 2.39 (1 H, t, *J* 6.5 Hz), 1.74 (4 H, m), and 1.15 (1 H, m); *m/e* 188 (71%, *M*$^+$), 187 (8), 173 (8), 171 (10), 160 (100), 147 (68), 132 (8), 131 (20), 115 (10), 105 (10), 103 (10), 91 (10), 85 (19), 84 (11), 83 (21), 77 (15), and 56 (22); *m** 136 (188 ⟶ 160) and 109 (160 ⟶ 132); phosphorescence max. 414 nm (emission from 360 to 550 nm). After 13 min. irradiation some starting material was present (n.m.r.); longer times of irradiation gave up to 48% of isolated product but it was more difficult to purify. Sensitisation with xanthen-9-one did not increase the yield of product or shorten the reaction time. With irradiation

through a Pyrex filter in the presence of xanthen-9-one, the photoreaction did not take place.

Tetracyclo[6.4.0.0^{2,4}.0^{3,7}]*dodeca*-1(8),9,11-*triene*-9,12-*diyl Diacetate* (2e).—The *diacetate* (2e) [obtained from (2d) by treatment with acetic anhydride and pyridine] crystallized from ethanol–water in needles, m.p. 109.5—110.5°; $\nu_{max.}$ 1 800—1 750, 1 615, and 1 580 cm^{-1}, δ (CDCl$_3$) 6.75 (2 H, AB, aromatic), 3.55 (1 H, t, *J* 5 Hz), 2.76 (1 H, dd, *J* 13 and 6.5 Hz), 2.26 (3 H, s, Ac), 2.22 (3 H, s, Ac), and 2.49—1.12br (6 H, series of multiplets); δ$_C$ (CDCl$_3$) 168.7 (Me*C*O), 144.4 (C-9), 142.6 (C-12), 141.5 (C-1), 136.2 (C-8), 120.5 (C-10 or -11), 119.6 (C-11 or -10), 46.6 (C-7), 41.6 (C-5), 38.7 (C-2), 30.8 (C-3), 29.4 (C-4), 22.5 (C-2), and 20.4 (*C*H$_3$·CO); phosphorescence $\lambda_{max.}$ 424 nm (emission from 360 to 510 nm) (Found: C, 70.7; H, 6.0. C$_{16}$H$_{16}$O$_4$ requires C, 70.55; H, 5.9%).

Bistetrahydropyranyl Ether (1i) *of the Diol* (1g).—The *ether* (1i), prepared from (1g) by the procedure used to prepare (1d), was obtained as prisms, m.p. 152—155° (30%); $\nu_{max.}$ 1 600 cm^{-1}; δ (CDCl$_3$) 6.81 (2 H, s, vinylic), 6.50 (2 H, m, aromatic), 5.28 (2 H, m, O·CH·O), 4.42 (2 H, m, bridge-head), 4.1—3.4 (4 H, m, O·CH$_2$·O), 2.0—1.5 (12 H, m, pyran ring), and 1.45 (2 H, m, bridge) (Found: C, 74.15; H, 7.95. C$_{22}$H$_{28}$O$_4$ requires C, 74.15; H, 7.85%).

1,4-*Dihydro*-[2,3,6,7-^{2}H$_4$]-1,4-*ethanonaphthalene*-5,8-*diol* (1h).—The ether (1i) was converted into the deuteriated compound (1h) as for the methano-derivative (1c). N.m.r. spectroscopy showed 60% replacement by deuterium. Repetition of the procedure gave material with 90% of hydrogen replaced by deuterium.

Irradiation of the [^{2}H$_4$]*Diol* (1h).—A solution of the diol (1h) (0.276 g) in ether (175 ml) was irradiated for 12 min with the 450 W lamp. Evaporation followed by work-up as for the non-deuteriated compound afforded the deuteriated compound (2f) as off-white crystals; δ [CDCl$_3$ and (CD$_3$)$_2$CO] 7.4 (s, OH), 6.50 (m, aromatic, reduced intensity), 3.70 (m), 2.60 (m, reduced intensity), 1.90 (m), and 1.25 (m). The ^{13}C n.m.r. spectrum of the diacetate (2g) was the same as that of (2e) except that the signals at δ$_C$ 38.7 and 30.8 were less intense and broadened in the spectrum of (2g).

Hydroquinone.—Hydroquinone had fluorescence (ether) $\lambda_{max.}$ 327 nm and phosphorescence $\lambda_{max.}$ (EtOH) 410 nm (emission from 360 to 520 nm), τ$_p$ 2.6 s; $\lambda_{max.}$ (ether) 417 nm, τ$_p$ 2.7 s.

X-Ray Crystal Structure Analysis of the Diacetate (2e).—Crystal data. C$_{16}$H$_{16}$O$_4$, *M* = 272.3. Orthorhombic, *a* = 8.37(2), *b* = 18.60(3), *c* = 9.49(2) Å, *U* = 1 477 Å^3, D_m = 1.23 (by flotation), *Z* = 4, D_c = 1.225, *F*(000) = 576. Cu-K_α radiation (λ 1.542 Å), μ = 7.3 cm^{-1}. Space group *Pnma*(D_{2h}^{16}) or *Pna2$_1$*(C_{2v}^9) with *b* and *c* axes interchanged, from systematic absences: 0*kl* when *k* + *l* ≠ 2*n*, *hk*0 when *h* ≠ 2*n*; concluded to be the former with a disordered structure from the refinement.

Crystallographic measurements. Unit cell dimensions were evaluated from rotation and Weissenberg photographs taken with Cu-K_α radiation and precision photographs taken with Mo-K_α (λ 0.7107 Å) radiation. Intensity data from the 0—7*kl* reciprocal lattice levels were recorded photographically using Cu-K_α radiation and the equi-inclination, multiple-film Weissenberg method. Intensities were estimated visually by comparison with a calibrated intensity strip. The strong reflections all showed large

[14] D. B. Denny and M. A. Greenbaum, *J. Amer. Chem. Soc.*, 1957, **79**, 3701.
[15] O. Diels and K. Alder, *Ber.*, 1929, **62**, 2337.

thermal diffuse scattering streaks. Corrections for spot-shape variation and Lorentz and polarization effects applied to these intensity estimates yielded 774 non-zero structure amplitudes which were used in the analysis. No allowance was made for the small absorption effects. Initially the various layers of data were assumed to be on a common scale as all had been given approximately equal exposure times. Absolute layer scales were derived at the end of the isotropic refinement stage by setting $K\Sigma|F_o| = \Sigma|F_o|$ for each layer.

Structure analysis. Of the two alternative space group choices based on systematic absences, only $Pna2_1$ can accommodate an ordered arrangement of four molecules since the molecule possesses neither a centre of symmetry nor a mirror plane of symmetry, either of which would be demanded by $Pnma$.

The structure was solved by application of direct phase-determining methods using the symbolic addition procedure with tangent formula refinement as described previously.[16] Reflections included in the starting set are given in the Supplementary Publication. A structure model compatible with the spectral data was obtained in part from an E-map and completed by a subsequent Fourier synthesis. The molecule was found to be oriented in the crystal such that pairs of atomic positions, except for C(4) and C(6), were related by a mirror plane of symmetry which bisected the C(10)–C(11) and C(1)–C(8) bonds and passed through C(3) and C(5). A Dreiding molecular model shows that reflection of C(4) and C(6) through this mirror plane produces images which differ from the original positions by <1.0 Å, and this separation would be decreased by thermal motion in the crystal. Thus the only major difference between $Pna2_1$ and $Pnma$ lies in the positions assigned to C(4) and C(6), the former space group requiring the presence of one enantiomer per equivalent position whereas the latter demands 50% site occupation by enantiomer pairs, *i.e.* a disordered

† For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin I*, 1975, Index issue.

structure. Numerous attempts to refine the structure model in $Pna2_1$ by combination of full-matrix least-squares calculations and Fourier syntheses did not lead to an unequivocal distinction between the two alternative space groups. Since there would be only a small difference in crystal packing between enantiomer pairs oriented in the manner found, we concluded that the structure was well suited for disorder and consequently the crystal was best considered as belonging to space group $Pnma$ (b and c axes interchanged to conform to International Tables).[17] Full-matrix least-squares refinement of positional and anisotropic thermal parameters for all the carbon and oxygen atoms, except C(4) and C(6) which were refined with isotropic thermal parameters by Fourier methods and included in the structure-factor calculations as half-weight atoms, was terminated at R 0.178. Final atomic co-ordinates, thermal parameters, and a list of observed and calculated structure factors are in Supplementary Publication No. SUP 21648 (11 pp., 1 microfiche).†

For all structure-factor calculations scattering factors for oxygen and carbon were taken from ref. 18 and for hydrogen the values from ref. 19 were used. The final least-squares weighting scheme $\sqrt{w} = (1.48 - 0.197 \ |F_o| + 0.0350 \ |F_o|^2)^{-\frac{1}{4}}$ was derived to produce no systematic dependence of $\langle w\Delta^2 \rangle$ when analysed in ranges of $|F_o|$.