

Autoxidation of Naphthols: A New Entry to the Perylene System

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Naphthols undergo autoxidation when adsorbed on silica gel and exposed to air, the main products being quinones. 2-Naphthol yields 4-(2-hydroxy-1-naphthyl)-1,2-naphthoquinone, and 4-methoxy-1-naphthol gives 4,4'-dimethoxy-2,2'-binaphthyl-1,1'-quinone. 1,1'-Binaphthyl-2,2',7,7'-tetrol turns blue on silica gel with formation of the anion of the tautomeric 6,7-dihydroxyperylene-1,12-quinone which is obtained more easily by autoxidation in aqueous solution. The same quinone can also be derived from naphthalene-2,7-diol in aqueous solution but on silica gel it forms the blue anion of 6,7-dihydroxy-3-(2,7-dihydroxy-1-naphthyl)perylene-1,12-quinone.

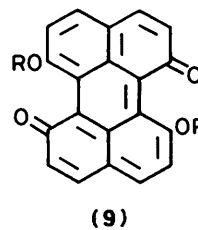
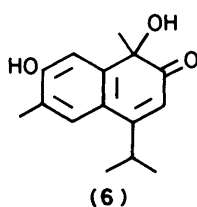
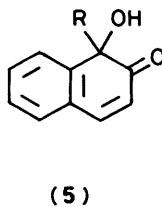
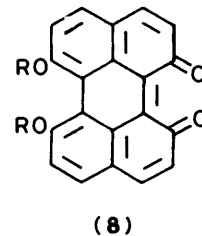
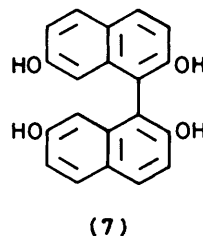
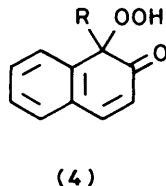
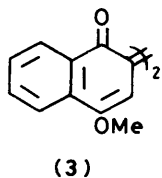
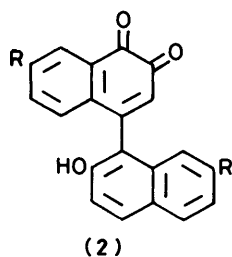
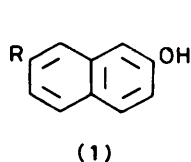
The use of oxidising agents supported on silica gel is well established.¹ Less attention has been paid to autoxidation on a silica surface although it is well known that substances left on t.l.c. plates are prone to oxidise when exposed to air.²

In the course of other work we noticed that naphthalene-2,7-diol turned blue when left on silica gel. That naphthols should autoxidise under these conditions is not surprising but the structure of the blue product was unexpected, and this led us to examine briefly the behaviour of other naphthols when exposed to air on silica gel. After 24 h, several compounds may be formed, mostly coloured, and sometimes in appreciable yield. For example, silica impregnated (1%) with 2-naphthol (**1**; R = H) becomes orange-pink, and the main product was identified as the *o*-quinone (**2**; R = H) (14%) which has also been obtained by the oxidation of 2-naphthol with hydrogen peroxide.³ Presumably (**2**; R = H) is responsible for the pink colour of old samples of 2-naphthol. Similarly (**1**; R = OMe) exposed to air on silica gel gave (**2**; R = OMe) as the main product. Whereas 2-naphthols yield predominantly one

compound, 1-naphthols tend to give mixtures of coloured products, an exception being 4-methoxy-1-naphthol which rapidly turns blue on silica with formation of Russig's Blue (**3**) (40%). Under the same conditions anthrone gave only anthraquinone.

It is known⁴ that 1-alkyl-2-naphthols will react with oxygen in solution, in the absence of catalysts or bases, to yield peroxides (**4**) and/or hydroxy ketones (**5**). Exceptionally, 1-methyl-2-naphthol does not react in that way, but when exposed to air on silica gel 4-isopropyl-1,6-dimethylnaphthalene-2,7-diol affords the hydroxy ketone (**6**) (lacidene C).⁵ Silica gel is normally slightly basic so that quinone formation presumably proceeds *via* the naphthoxide which reacts with oxygen to give first the corresponding naphthoxyl and then the hydroperoxide (**4**; R = H) followed by base-catalysed dehydration. The resulting 1,2-quinone then undergoes nucleophilic attack by adjacent molecules of 2-naphthol to form the final product (**2**) after further oxidation. The formation of bimolecular products will be concentration-dependent. (The possibility that (**2**) might be formed while extracting the products from silica gel was discounted by stirring a mixture of equal amounts of 2-naphthol and 1,2-naphthoquinone in a suspension of silica gel in methanol; after 1 h (**2**; R = H) could not be detected).

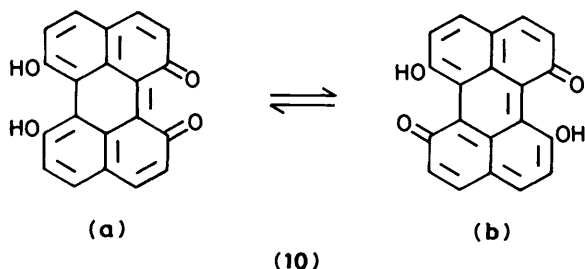
The most interesting examples are our original naphthalene-2,7-diol (**1**; R = OH) and its dehydro dimer (**7**). When these are adsorbed, separately, onto silica gel and exposed to air, the silica



becomes pale blue but different products are formed. The deep blue-black, highly polar solid derived from (7) gave rather poor ^1H n.m.r. and mass spectra which were difficult to reproduce. Accordingly, the material was subjected to methylation and acetylation which yielded two isomeric violet-red dimethyl ethers, and two red diacetates, respectively.

The dimethyl ethers, $\text{C}_{22}\text{H}_{14}\text{O}_4$, showed simple ^1H n.m.r. spectra consisting of two pairs of 2H doublets ($J \sim 9$ Hz) in the region δ 7.7—6.5, and a methoxy singlet (6H) close to δ 4. The dimethyl ethers can, therefore, be represented by structures (8) and (9) ($R = \text{Me}$). Analogous spectra were obtained for the diacetates (8) and (9) ($R = \text{Ac}$). One of the dimethyl ethers shows λ_{max} 556 nm and ν_{CO} 1630 cm^{-1} , and the other λ_{max} 537 nm and ν_{CO} 1652 cm^{-1} . The latter data are tentatively attributed to (8; $R = \text{Me}$) on the assumption that steric crowding will be greater than in (9; $R = \text{Me}$) resulting in more distortion of the molecule and reduced conjugation. These assignments are also consistent with the higher $M^+ + 2/M^+$ ion intensity ratio in the mass spectrum of (8; $R = \text{Me}$) relative to that of (9; $R = \text{Me}$). The two diacetates can be identified similarly on the basis of their i.r. and visible spectra.

At this stage it appeared that the blue product obtained from (7) was the tautomeric dihydroperylenequinone (10) but the

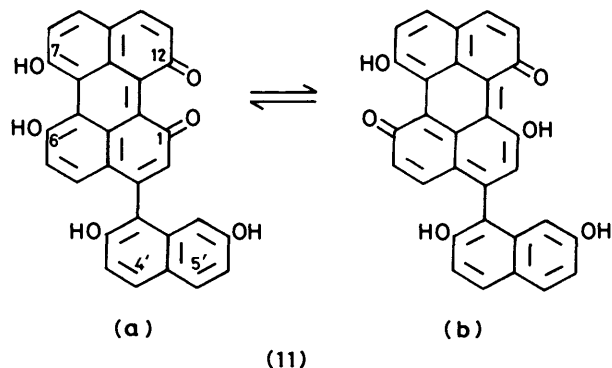


material was surprisingly soluble in water and chromatographed as a highly ionized material. In fact, the blue substance is an anion which is formed on basic silica gel, and when (7) is applied to acid-washed silica a blue colour does not develop. Acidification of the blue material in aqueous solution gave a dark green precipitate, isolated eventually as a black powder insoluble in water and methanol but soluble (with difficulty) in chloroform to give a green solution (λ_{max} 694 nm). On spotting the green solution onto silica gel it immediately turns blue. The ^1H n.m.r. spectrum of this compound consists of two 4H doublets at $\delta[(\text{CD}_3)_2\text{SO}]$ 7.90 and 6.85 (J 9 Hz) (OHs not observed) consistent with the tautomeric quinone structure (10). It forms a leucotetra-acetate showing a perylene-type u.v.-visible spectrum and a blue fluorescence in solution.

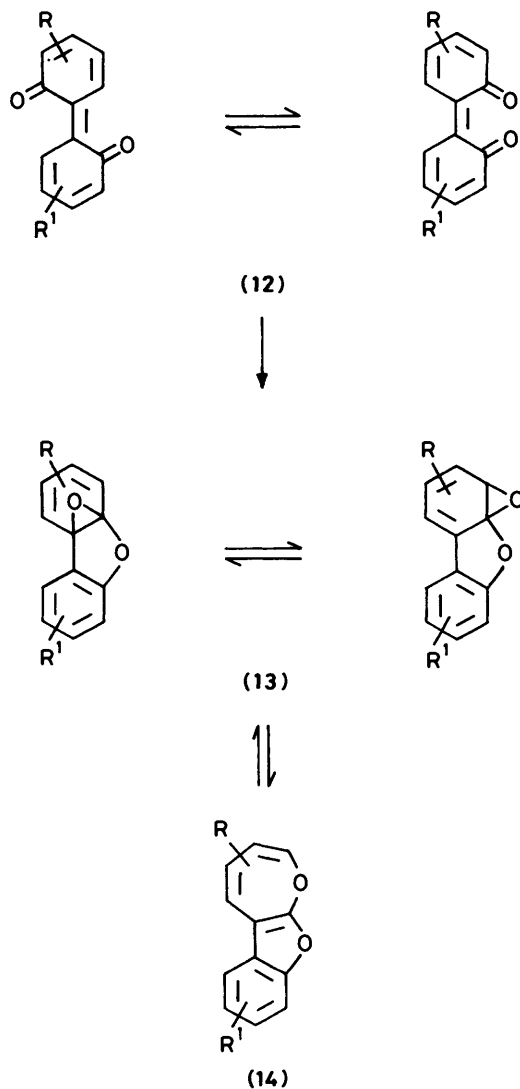
The quinone (10) is obtained more easily from (7) by stirring a 0.05% aqueous solution, containing 1 equivalent of sodium hydroxide, exposed to air for 12 h. The yield is 36%, in marked contrast to the 1—2% obtained on silica gel. The latter is consistent with the small proportion of the binaphthyl held on the silica surface in the least favourable co-planar conformation (7), which is essential for the formation of the perylene system by phenolic coupling. The 36% yield obtained in solution could probably be increased at higher dilution. If the oxidation at 0.05% concentration is continued an additional red compound is formed, the solution becoming violet and eventually deep purple. The perylenequinone (10) can also be obtained by autoxidation of naphthalene-2,7-diol (1; $R = \text{H}$) in dilute aqueous solution; the yield after 9 h was 16%.

Although (1; $R = \text{OH}$) gave (10) in 0.1% aqueous solution the original blue product obtained by autoxidation on silica gel (1% concentration) was trimeric. Acidification of its aqueous solution again gave a dark green precipitate, finally isolated as a

black powder. It dissolves slowly in chloroform to give a green solution, and also forms a violet solution in methanol which turns blue on addition of water. This product is formulated as (11) (or another tautomer). Its electronic spectrum is similar to



that of (10), and it yields a yellow leucohexa-acetate similar to the leucotetra-acetate of (10). The ^1H n.m.r. spectrum $[(\text{CD}_3)_2\text{SO}]$ confirms the presence of 12 ring protons of which nine are *o*-coupled, one is *m*-coupled, one *o*- and *m*-coupled, and one is a singlet at δ 6.83. The only possible, but chemically unlikely, alternative structure would have the dihydroxy-



naphthyl 'substituent' at C-2. The lone proton would then be 3-H and would be expected to resonate at lower field.

The C₃₀ quinone must be formed from (1; R = OH) by double phenolic coupling to form a perylene-tetrol followed by further oxidation to the quinone level, nucleophilic addition of (1; R = OH), and final oxidation. The yield (10–15%) of (11) is substantially higher than that of (10), when derived from (7) on silica gel, showing that a significant proportion of (1; R = OH) molecules lie on the silica surface in the 'head-to-head' coplanar arrangement required for the formation of the perylene system.

As the tautomeric quinone (11) is unsymmetrical, on methylation it gives a mixture of four tetramethyl ethers. Two of these could be separated. They have almost identical u.v.-visible and i.r. spectra showing ν_{CO} 1 650 cm⁻¹ which suggests, by comparison with (10), that they are derivatives of (11a) and its 1,12-dihydroxy-6,7-quinone isomer.

Mass Spectra.—The mass spectrum of (10) is unusual in that it includes a peak at m/z 298.0597 corresponding to C₂₀H₁₀O₃, i.e. M⁺ - O. The same feature is observed in the spectra of the diacetates (following the loss of two molecules of ketene). The perylenequinones which exist in the form (10a) or (11a) can be regarded as annelated *cis*-locked *o,o'*-diphenoquinones. *o,o'*-Diphenoquinones (12) are of limited stability and the *E*-configuration is preferred.⁶ Generally they rearrange in solution *via* the *Z*-forms (a mechanism for the *E* \rightleftharpoons *Z* equilibrium has been proposed⁶) to give stable oxepinobenzofurans (14) as indicated.⁷ We suggest that (10a) partly isomerises on the probe to benzene oxide structures [corresponding to (13)] which fragment with loss of oxygen.

Neither of the dimethyl ethers (8) and (9) (R = Me) appeared to fragment by deoxygenation. The same is true of the tetramethyl ethers of (11) (the spectra were very weak) while (11) itself gave very poor spectra which were difficult to reproduce. The mass peak M⁺(472) was usually absent and in several samples the highest (and very weak) peak was at m/z 440.

Experimental

Autoxidations and p.l.c. were run on Kieselgel 60 GF₂₅₄ (Merck), and silica gel Grade 62 (Grace) was used for dry columns. U.v. spectra were recorded on a Perkin-Elmer 402 instrument and i.r. spectra on a P.E. 197 spectrophotometer. ¹H N.m.r. spectra were measured in CDCl₃ (unless otherwise stated) at 220 MHz on a Perkin-Elmer R34 spectrometer and at 360 MHz on a Bruker WH 360 instrument. Mass spectra were obtained using an A.E.I. MS 30 mass spectrometer at 70 eV. M.p.s were determined on a Kofler block. Light petroleum refers to the fraction b.p. 60–80 °C.

Autoxidations: General Procedure.—The naphthol (150 mg) was adsorbed onto silica gel (15 g) (from acetone or methanol), and then spread on a sheet of paper as a thin layer, and left exposed to air. After 24 h the silica was extracted with cold acetone or methanol, and evaporated. The residue was purified by chromatography.

(i) *2-Naphthol*. The crude product, after p.l.c. in chloroform, crystallised from benzene as dark red needles, m.p. 148–149 °C (lit.,^{3a} 148 °C) (14%), identical (t.l.c., m.s., and i.r.) with authentic 4-(2-hydroxy-1-naphthyl)-1,2-naphthoquinone (2; R = H).

(ii) *7-Methoxy-1-naphthol*. After p.l.c. in chloroform–acetone (19:1) followed by chloroform–methanol (19:1), 4-(2-hydroxy-7-methoxy-1-naphthyl)-7-methoxy-1,2-naphthoquinone (2; R = OMe) crystallised from dichloromethane–light petroleum as dark red plates, m.p. 237–240 °C (13%) (Found: C, 73.0; H, 4.5%; M⁺, 360.0953. C₂₂H₁₆O₅ requires C, 73.3; H, 4.5%; M, 360.0997); λ_{max} (MeOH) 239, 272, and 462 nm (log ϵ 4.79, 4.41, and 3.48); ν_{max} (CHCl₃) 3 560, 1 663, 1 622, and 1 600 cm⁻¹; δ

7.81–7.68 (3 H, m, ArH), 7.10–6.69 (5 H, m, ArH), 6.43 (1 H, s, QH), 5.40br (1 H, s, OH), and 3.86 and 3.70 (each 3 H, s, OMe); m/z (%) (362 (100), 360 (M⁺, 28), 332 (83), 317 (26), 301 (100), 273 (23), 189 (26), 150 (18), and 95 (17).

(iii) *4-Methoxy-1-naphthol*. The silica gel became dark blue and was extracted with chloroform after 16 h. The residue was passed down a column of dry silica in chloroform, and the blue fraction was crystallised from benzene–light petroleum to give 4,4'-dimethoxy-2,2'-binaphthyl-1,1'-quinone as blue-violet needles, m.p. 256–258 °C (lit.,⁸ 256–258 °C) (40%) identical (t.l.c., m.s., and i.r.) with an authentic sample.

(iv) *Anthrone*. The crude product crystallised from toluene as pale yellow needles, m.p. 285–287 °C (lit.,⁹ 286 °C) (80%) identical (t.l.c., mixed m.p., and i.r.) with 9.10-anthraquinone.

6,7-Dihydroxyperylene-1,12-quinone (10).—(a) After autoxidation of 1,1'-binaphthyl-2,2',7,7'-tetrol (300 mg) on silica gel in the usual way, extraction with methanol gave a residue which was chromatographed (twice) on a dry column of silica in methanol–chloroform (3:7) and then passed down a column of Sephadex LH 20 in methanol. The resulting blue-black solid [λ_{max} (MeOH) 332 and 610 nm] was dissolved in methanol (10 ml) and water (90 ml), and acidified with 2M-hydrochloric acid. The dark-green, flocculent precipitate was allowed to settle, the supernatant decanted, and the suspension collected by centrifugation and washed with water. After being dried *in vacuo* the solid was extracted briefly with boiling methanol, and again dried to give (10) as a black powder (1–2%) (Found: C, 76.0; H, 3.2%; M⁺, 314.0569. C₂₀H₁₀O₄ requires C, 76.4; H, 3.2%; M, 314.0579); λ_{max} (CHCl₃) 294, 327, and 694 nm (log ϵ 4.42, 4.45, and 3.73); ν_{max} (KBr) 1 626 cm⁻¹; δ [(CD₃)₂SO] 7.90 and 6.85 (each 4 H, d, *J* 9 Hz); m/z (%) 316 (27), 315 (26), 314 (M⁺, 100), 299 (46), 298.0597 (C₂₀H₁₀O₃ requires 298.0628, 41), 286 (75), 282 (11), 258 (22), 229 (11), 213 (13), and 200 (11).

(b) To a stirred solution of 1,1'-binaphthyl-2,2',7,7'-tetrol (100 mg) in methanol (10 ml) and water (190 ml) was added 2M-sodium hydroxide (0.32 ml). After 12 h the blue solution was acidified (2M-HCl). The dark green precipitate was allowed to settle and worked up, as before, to give (10) as a black powder (36 mg, 36%) identical with that obtained in (a).

(c) As for (b) using naphthalene-2,7-diol (300 mg) in methanol (30 ml) and water (270 ml). The solution was acidified after 9 h and worked up as above; yield 48 mg (16%). The supernatant liquid was a pale brownish pink and the hot methanolic extract was light red.

The *leucotetra-acetate* (Ac₂O–Zn–Et₃N) was purified by p.l.c. (in the dark) in ethyl acetate–light petroleum (1:1) and then chloroform, and crystallised from methylene dichloride–light petroleum at –10 °C as pale brown needles, m.p. 282–284 °C (Found: M⁺, 484.1152. C₂₈H₂₀O₈ requires M, 484.1158); λ_{max} (MeOH) 269, 397, and 408 nm; ν_{max} (CHCl₃) 1 760 cm⁻¹; m/z (%) 484 (M⁺, <1), 442 (1), 400 (2), 382 (10), 358 (4), 340 (6), 316 (7), and 298 (100).

Methylation (Me₂SO₄–K₂CO₃–Me₂CO) gave two *dimethyl ethers* which were separated by p.l.c. in chloroform–methanol (19:1). Isomer (8; R = Me) formed dark red needles, m.p. 277–279 °C (dichloromethane–methanol) (Found: M⁺, 342.0891. C₂₂H₁₄O₄ requires M, 342.0892); λ_{max} (CHCl₃) 254, 331, and 537 nm (log ϵ 3.82, 3.98, and 3.32); ν_{max} (CHCl₃) 1 652 and 1 625 cm⁻¹; δ 7.67 and 7.15 (each 2 H, d, *J* 9 Hz), 7.57 and 6.58 (each 2 H, d, *J* 10 Hz), and 4.08 (6 H, s, OMe); m/z (%) 344 (54), 343 (25), 342 (M⁺, 7), 329 (10), 312 (18), 311 (17), and 172 (10). Isomer (9; R = Me), dark red microcrystals, m.p. 285–290 °C (decomp.) (dichloromethane–light petroleum) (Found: M⁺, 342.0891. C₂₂H₁₄O₄ requires 342.0892); λ_{max} (CHCl₃) 312, 364sh, and 556 nm (log ϵ 4.29, 3.75, and 3.87); ν_{max} (CHCl₃) 1 630 and 1 615 cm⁻¹; δ 7.70 and 7.02 (each 2 H, d, *J* 9 Hz), 7.61 and 6.66 (each 2 H, d, *J* 10 Hz), and 4.03 (6 H, s, OMe); m/z (%), 344 (62), 342

(M^+ , 27), 329 (74), 325 (55), 308 (72), 307 (30), 297 (23), 286 (22), 213 (33), 200 (24), and 172 (12).

Acetylation ($\text{Ac}_2\text{O}-\text{NaOAc}$) gave two diacetates which were separated by p.l.c. in ether. Isomer (9; $\text{R} = \text{Ac}$), crystallised from dichloromethane-methanol as red plates, decomp. $> 280^\circ\text{C}$ (Found: M^+ , 398.0789. $\text{C}_{24}\text{H}_{14}\text{O}_6$ requires M , 398.0790); $\lambda_{\text{max.}}(\text{CHCl}_3)$ 280 and 524 nm ($\log \epsilon$ 4.34 and 3.69); $\nu_{\text{max.}}(\text{CHCl}_3)$ 1 770, 1 632, and 1 621 cm^{-1} ; δ 7.84 and 7.56 (each 2 H, d, J 9 Hz), 7.74 and 6.78 (each 2 H, d, J 10 Hz), and 2.32 (6 H, s, OAc); m/z (%) 400 (16), 398 (M^+ , 1), 358 (15), 316 (100), 315 (49), 314 (26), 298.0568 ($\text{C}_{20}\text{H}_{10}\text{O}_3$ requires 314.0578, 40), 297 (24), 286 (13), 286 (16), 270 (9), and 213 (16). Isomer (8; $\text{R} = \text{Ac}$), red plates, m.p. 218–219 $^\circ\text{C}$ (decomp.) (dichloromethane-methanol) (Found: $M^+ + 2$, 400.0948. $\text{C}_{24}\text{H}_{16}\text{O}_6$ requires 400.0946); $\lambda_{\text{max.}}(\text{CHCl}_3)$ 331 and 480 nm ($\log \epsilon$ 4.25, and 3.71), $\nu_{\text{max.}}(\text{CHCl}_3)$ 1 765, 1 660, and 1 630 cm^{-1} ; δ 7.72 and 7.48 (each 2 H, d, J 9 Hz), 7.60 and 6.67 (each 2 H, d, J 10 Hz), and 2.30 (6 H, s, OAc); m/z (%) 400 ($M^+ + 2$, 14), 358 (18), 356 (6), 316 (100), 315 (55), 314.0549 ($\text{C}_{20}\text{H}_{10}\text{O}_4$ requires 314.0578, 30), 298.0643 ($\text{C}_{20}\text{H}_{10}\text{O}_3$ requires 298.0628, 24), 297 (15), 286 (21), 282 (9), 270 (18), and 213 (30).

6,7-Dihydroxy-3-(2,7-dihydroxy-1-naphthyl)perylene-1,12-quinone (11).—Autoxidation of naphthalene-2,7-diol on silica gel was carried out and worked up as for (10) except that the final residue was not extracted with hot methanol; black powder (14%) (Found: C, 76.0; H, 3.5%; M^+ , 472. $\text{C}_{30}\text{H}_{16}\text{O}_6$ requires C, 76.3; H, 3.4%; M , 472); $\lambda_{\text{max.}}(\text{CHCl}_3)$ 294, 332, 392sh, and 696 nm ($\log \epsilon$ 4.39, 4.45, 3.96, and 3.72); $\nu_{\text{max.}}(\text{KBr})$ 1 622 cm^{-1} ; $\delta[(\text{CD}_3)_2\text{SO}]$ 9.6 (2 H, v br, naphthyl OH), 7.97 (2 H, d, J 8.4 Hz, 8- and 11-H), 7.80 (1 H, d, J 8.8 Hz, 4'-H), 7.74 (1 H, J 8.8 Hz, 5'-H), 7.26 (1 H, d, J 9.1 Hz, 4-H), 7.13 (1 H, d, J 8.8 Hz, 3'-H), 7.01 (1 H, d, J 8.4 Hz, 9- or 10-H), 6.92 (1 H, d, J 8.4 Hz, 10 or 9-H), 6.86 (1 H, dd, J 8.8 and 2.1 Hz, 6'-H), 6.83 (1 H, s, 2-H), 6.75 (1 H, d, J 9.1 Hz, 5-H), and 6.57 (1 H, d, J 2.1 Hz, 8'-H); $2 \times \text{OH}$ not observed.

The leucohexa-acetate ($\text{Ac}_2\text{O}-\text{Zn}-\text{Et}_3\text{N}$) was purified by p.l.c. in chloroform-acetone (96:4), and then crystallised from ether at -10°C to give yellow sheaves, m.p. 169–171 $^\circ\text{C}$ (Found: C, 69.7; H, 4.2. $\text{C}_{42}\text{H}_{30}\text{O}_{12}$ requires C, 69.4; H, 4.2%); $\lambda_{\text{max.}}(\text{MeOH})$ 271.5, 399, and 422 nm ($\log \epsilon$ 4.56, 4.23, and 4.29); $\nu_{\text{max.}}(\text{CHCl}_3)$ 1 760 cm^{-1} ; δ 8.02–7.80 (4 H, m, ArH), 7.60–7.05 (8 H, m, ArH), and 2.35, 2.30, 2.26, 2.23, 2.18, and 1.91 (each 3 H, s, OAc); m/z (%) 726 (M^+ , 17), 684.1659 ($\text{C}_{40}\text{H}_{28}\text{O}_{11}$ requires 684.1629, 16), 642.1544 ($\text{C}_{38}\text{H}_{26}\text{O}_{10}$ requires 642.1523, 35), 600 (39), 558 (100), 516 (9), 515 (14), 478 (8), 456 (13), and 455 (15).

The tetramethyl ethers ($\text{Me}_2\text{SO}_4-\text{K}_2\text{CO}_3-\text{Me}_2\text{CO}$) were separated by p.l.c. in chloroform, the main violet band being collected and separated into two components (A) and (B) by further chromatography (twice) in ethyl acetate-ether (9:1). (A) Was a mixture of two isomers which were finally separated by further p.l.c. in chloroform-ether (9:1), with multiple development, to give (A_1) as dark violet micro-needles, m.p.

212–214 $^\circ\text{C}$ (dichloromethane-light petroleum) (Found: $M^+ + 2$, 530.1765. $\text{C}_{34}\text{H}_{26}\text{O}_6$ requires 530.1727); $\lambda_{\text{max.}}(\text{MeOH})$ 238, 331, and 552 nm; $\nu_{\text{max.}}(\text{CHCl}_3)$ 1 650 and 1 627 cm^{-1} ; δ 7.88, 7.74, 7.66, and 7.58 (each 1 H, d, J 9 Hz), 7.45–6.85 (6 H, m), 6.63 (1 H, d, J 10 Hz), 6.60 (1 H, s), and 4.08, 4.00, 3.81, and 3.62 (each 3 H, s); m/z (%) (530 ($M^+ + 2$), 515, 514, 499, 498, and 482 (all v. weak); and isomer (A_2) dark violet microcrystals, m.p. 182–184 $^\circ\text{C}$ (ether) (Found: $M^+ + 2$, 530.1724. $\text{C}_{34}\text{H}_{26}\text{O}_6$ requires 530.1727); $\lambda_{\text{max.}}(\text{MeOH})$ 238, 331, and 552 nm; $\nu_{\text{max.}}(\text{CHCl}_3)$ 1 651 and 1 627 cm^{-1} ; δ 7.93, 7.78, 7.68, and 7.58 (each 1 H, d, J 9 Hz), 7.3–7.0 (5 H, m), 6.62 and 6.40 (each 1 H, d, J 10 Hz), 6.59 (1 H, s), and 4.12, 4.03, 3.83, and 3.59 (each 3 H, s); m/z 530 ($M^+ + 2$), 515, 514, 499, 498, and 482 (all v. weak); (B) a dark violet solid, was a mixture of two isomers not separated by further chromatography (Found: $M^+ + 2$, 530.1741); $\lambda_{\text{max.}}(\text{MeOH})$ 237, 300, and 578 nm; $\nu_{\text{max.}}(\text{CHCl}_3)$ 1 629 and 1 614 cm^{-1} ; δ 7.95–6.44 (2 H, m) and 4.07, 4.03, 3.98, 3.96, 3.84, 3.83, 3.61, and 3.58 (each 3 H, s).

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