Oxidation of Bis-(2-hydroxy-1-naphthyl)methane with 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone. *X*-Ray Crystal Structure of a Novel Product

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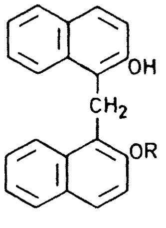
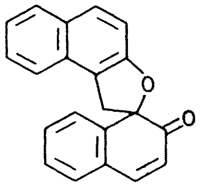
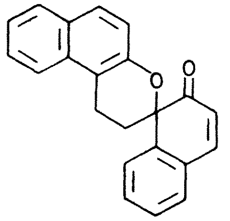
Summary A novel compound obtained by the oxidation of the title compound with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone has been assigned structure (**5**) on the basis of spectral data and *X*-ray crystal structure analysis.



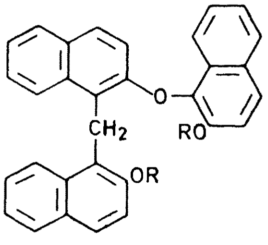
(1)
a; R = H
b; R = Me



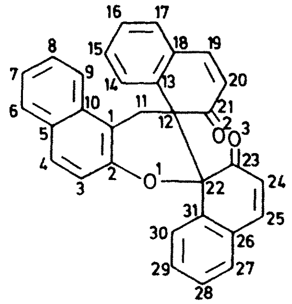
(2)



(3)



(4)
a; R = H
b; R = Me



(5)

In continuation of our studies on the oxidation of naphthols with quinones,[1] the oxidation of bis-(2-hydroxy-l-naphthyl) methane (**1a**) with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was carried out. The structure of a novel, unexpected product obtained in this reaction is reported herein.

The dinaphthol (**1a**, 1 mol) was oxidised with DDQ (1 mol) in refluxing benzene for 8 h. The neutral product obtained after the usual work-up was separated into less polar (30%, benzene as eluant) and more polar (35%, chloroform as eluant) fractions by column chromatography (neutral alumina). The less polar fraction, after purification by repeated preparative t.l.c. [silica gel, benzene–hexane (1 : 1)], was shown (t.l.c. and spectral data) to consist of the expected intramolecularly coupled product (**2**) and the known dimer (**3**) of 1,2-naphthoquinone-l-methide in the ratio 1 : 1.

The chloroform fraction, on further purification by column chromatography followed by crystallisation, gave a yellow solid,† m.p. 170 °C. Hydrogenation of this compound resulted in the formation of a dihydro-derivative (*m/e* 442). Structures (**4a**) and (**4b**), assigned respectively to the dihydro- and corresponding dimethoxy-compounds from a study of their ^1H and ^{13}C n.m.r spectra, were further corroborated by an unambiguous synthesis involving coupling of (**1b**) with 1-bromo-2-methoxynaphthalene, followed by demethylation.

On the basis of the spectroscopic data,† the unusual dispirodienone structure (**5**) was tentatively assigned to the oxidation product.

Results obtained from *X*-ray structure analysis of the above compound are in full agreement with the structure proposed. It crystallised from $CHCl_3$–hexane (1 : 1) as yellow needles solvated with chloroform.

Crystal data: $C_{31}H_{20}O_3$, $M = 440$, monoclinic, space group $P2_1/n$, $a = 7{\cdot}901(2)$, $b = 17{\cdot}475(13)$, $c = 19{\cdot}637(16)$ Å, $\beta = 101{\cdot}43(4)°$, $U = 2659{\cdot}8$ Å^3, $Z = 4$, $D_c = 1{\cdot}410$ g cm^{-3}, $D_m = 1{\cdot}40$ g cm^{-3}. The structure was solved by direct methods using MULTAN.[2] Least-squares refinement of atomic positional and thermal parameters (anisotropic C,O,Cl; isotropic H) reduced *R* to a current value of 0·117 for 2309 statistically significant [$F \geqslant 2{\cdot}00\ \sigma(F)$] reflections measured with a crystal enclosed in a Lindemann capillary tube on an Enraf–Nonius CAD-4 diffractometer (Zr-filtered

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† Spectroscopic data: *m/e* 440; λ_{max} ($CHCl_3$) 247 (ϵ 30,210), 262 (21,710), 268 (18,190), 280 (12,310), 294 (9380), 312 (7920), 320 (8210), and 348 nm (7330); ν_{max} (Nujol): 1690 and 1670 cm^{-1} (conj. C=O); ^1H n.m.r. δ ($CDCl_3$; Me_4Si) 3·27 (d, *J* 18 Hz, 1H), 4·29 (d, *J* 10 Hz, 1H), 5·83 (d, *J* 10 Hz, 1H), 6·0 (d, *J* 10 Hz, 1H), 6·34 (d, *J* 10 Hz, 1H), 6·77—6·80 (m, 2H), 6·9 (d, *J* 10 Hz, 1H), 7·0—7·27 (m, 7H), 7·39 (t, *J* 10 Hz, 1H), 7·49 (t, *J* 10 Hz, 1H), 7·77 (d, *J* 10 Hz, 1H), and 7·87 (br.d, *J* 10 Hz, 2H); ^{13}C n.m.r. (off-resonance decoupled) singlets at 56, 82, 113, 127·40, 131·74, 132·17, 136, 136·5, 140·27, 152, 199, and 200; doublets at 117·47, 122·17, 122·77, 123·54, 126·10, 126·40 (2C), 127·78, 127·93, 128·69 (3C), 129·12, 129·39, 129·48, 129·97, 141·40, and 144·85; triplet at 26·58 p.p.m.

Mo-K_α radiation, θ—2θ scans). A view of the molecular structure of compound (**5**) (excluding the $CHCl_3$ molecule) down the crystallographic *a* axis is shown in the Figure‡.

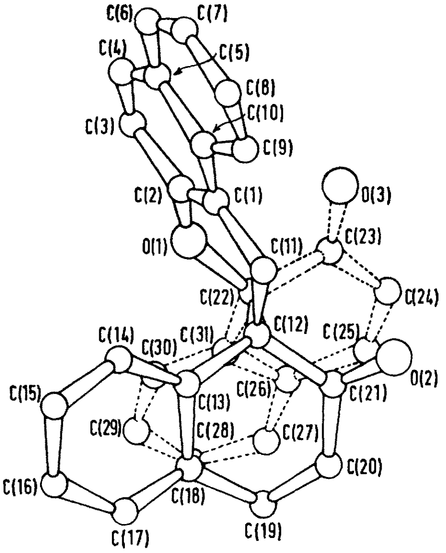
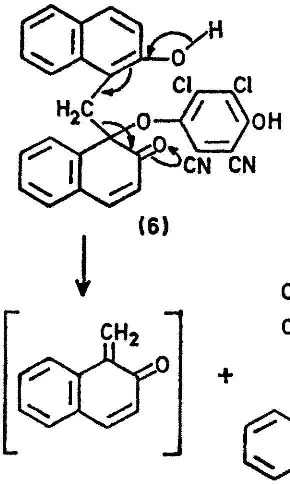


FIGURE. Molecular structure of compound (**5**) (excluding the $CHCl_3$ molecule of crystallisation) as viewed down the crystallographic *a* axis.

It is not very clear, at present, how this novel product is formed. Perhaps the quinol ether (**6**), initially formed, undergoes fragmentation[1] to give the dimer (**3**) of 1,2-naphthoquinone-1-methide and the naphthol (**7**) (Scheme). Further coupling of (**7**) with (**1a**), followed by elimination of the hydroquinone moiety, would result in the formation of (**5**).



(**6**)

(**7**)

SCHEME.

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[1] T. R. Kasturi, B. Rajasekhar, and R. Sivaramakrishnan, *Indian J. Chem.*, *Sect. B*, 1979, **18**, 1 and references therein.
[2] G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr.*, *Sect. A*, 1971, **27**, 368.