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# The Crystal and Molecular Structure of 5α,8α-Dimethyl-4aβ,5,8,8aβ-tetrahydro-1,4-naphthoquinone and its Solid-State Photodimer

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Crystals of 5α,8α-dimethyl-4aβ,5,8,8aβ-tetrahydro-1,4-naphthoquinone are monoclinic, space group $P2_1/c$, with $a = 7\cdot189\,(1)$, $b = 22\cdot241\,(4)$, $c = 6\cdot843\,(1)$ Å, $\beta = 106\cdot51\,(1)°$ and $Z = 4$. The molecules occur in pairs related by centres of symmetry, and irradiation of the crystals with ultraviolet light causes linking of the pairs to form dimers. Crystals of the product also have space group $P2_1/c$, with $a = 11\cdot393\,(1)$, $b = 8\cdot029\,(1)$, $c = 10\cdot771\,(5)$ Å, $\beta = 91\cdot04\,(1)°$ and $Z = 2$. The dimer molecule has a crystallographic centre of symmetry and a planar four-membered ring. In both molecules the fused six-membered rings have the 'twist' conformation observed for other cis-4a,5,8,8a-tetrahydro-1,4-naphthoquinones.

## Introduction

A study of the photochemistry of various substituted cis-4a,5,8,8a-tetrahydro-1,4-naphthoquinone derivatives in solution (Scheffer, Jennings & Louwerens, 1976) has revealed unusual reaction pathways. Irradi-

ation of the same derivatives in the crystalline state produces, in some cases, differing product ratios and even entirely different products (Dzakpasu, Phillips, Scheffer & Trotter, 1976). Photolysis of 5α,8α-dimethyl-4aβ,5,8,8aβ-tetrahydro-1,4-naphthoquinone (I) in solution results in abstraction of a methyl H by

carbonyl O, and collapse of the resulting diradical to form a tricyclic product (II).
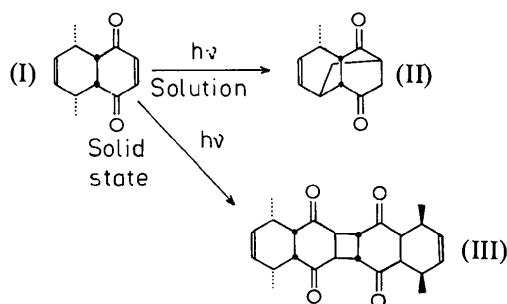


In the crystalline state, however, (II) is not formed but dimerization takes place to produce (III) exclusively.

## Experimental

### $5\alpha,8\alpha$-Dimethyl-$4\alpha\beta,5,8,8\alpha\beta$-tetrahydro-1,4-naphtho-quinone

Large yellow crystals of (I) were obtained by crystallization from a mixture of petroleum spirit and diethyl ether. A crystal (dimensions $ca$ $0.04 \times 0.07 \times 0.10$ cm) was mounted on a Datex-automated GE XRD 6 diffractometer with its $c^*$ axis parallel to the $\varphi$ axis of the goniometer. Accurate unit-cell constants were obtained by least-squares refinement with the $2\theta$ values of 18 manually centred reflexions.

Crystal data: $C_{12}H_{14}O_2$, FW 190.24, monoclinic, $a = 7.189$ (1), $b = 22.241$ (4), $c = 6.843$ (1) Å, $\beta = 106.51$ (1)°; $V = 1049.0$ (3) Å$^3$, $d_m = 1.18$ (flotation), $d_x = 1.204$ g cm$^{-3}$, $Z = 4$. Space group $P2_1/c$ ($0k0$, $k = 2n$; $h0l$, $l = 2n$). Cu $K\alpha$ radiation, Ni-filtered; $\lambda$(Cu $K\alpha$) = 1.5418 Å, $\mu$(Cu $K\alpha$) = 6.6 cm$^{-1}$.

Intensities were collected with the $\theta$–$2\theta$ scan technique, a scan speed of 4° min$^{-1}$ and 10 s background counts, to a maximum $2\theta$ of 120°. One standard reflexion, $2,\overline{14},1$, was measured after every fifty observations and its intensity fell by 16% during the data collection, the data being scaled accordingly. The cause was probably sublimation, as the crystal was smaller after the data collection, and the surface was visibly damaged. Of the 1557 independent reflexions collected, 1362 had intensities greater than $3\sigma(I)$ above background $[\sigma^2(I) = S + B + (0.06S)^2$, where $S = $ scan and $B = $ background count]. Lorentz and polarization corrections were applied and the structure amplitudes derived. No absorption correction was applied in view of the low value of the absorption coefficient and difficulty in defining the crystal dimensions.

### Photodimer III (5,8,15,18-*tetramethylpenta-cyclo*[10.8.0.0$^{2,11}$.0$^{4,9}$.0$^{14,19}$]*eicosa*-6,16-*diene-3,10,13,20-tetrone*)

Small, colourless plates were obtained by recrystallization from a mixture of chloroform and hexane. The sample chosen for data collection (dimensions $ca$ $0.040 \times 0.025 \times 0.010$ cm) was mounted on the diffractometer with the $\varphi$ axis through (011). Cell constants were refined from $2\theta$ values of 17 reflexions.

Crystal data: $C_{24}H_{28}O_4$, FW 380.48, monoclinic, $a = 11.393$ (1), $b = 8.029$ (1), $c = 10.771$ (5) Å, $\beta = 91.04$ (1)°; $V = 985.1$ (5) Å$^3$, $d_m = 1.28$ (flotation), $d_x = 1.283$ g cm$^{-3}$, $Z = 2$. Space group $P2_1/c$. Cu $K\alpha$ radiation, Ni-filtered; $\mu$(Cu $K\alpha$) = 7.0 cm$^{-1}$.

Intensities were collected as before, but with a scan speed of 2° min$^{-1}$. The standard reflexion, $61\overline{1}$, fluctuated randomly between limits of $\pm3.5\%$ during the data collection. Of the 1458 independent reflexions with $2\theta < 120°$, 1003 had intensities greater than $3\sigma(I)$ above background $[\sigma(I)$ defined as before but with the constant set to 0.05]. The structure amplitudes were derived as before and no absorption correction was applied.

## Structure determination and refinement

### $5\alpha,8\alpha$-Dimethyl-$4\alpha\beta,5,8,8\alpha\beta$-tetrahydro-1,4-naphtho-quinone

A Wilson plot gave good centric statistics and 201 $E$ values greater than 1.5 were derived. An automatic computer program (Long, 1965), applying a multi-solution procedure, was used to assign phases to the $E$ values. The set of phases with the highest consistency was used to calculate an $E$ map, which revealed the positions of all non-hydrogen atoms. Two cycles of isotropic, followed by two cycles of anisotropic, full-matrix least-squares refinement were carried out, where the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, with weights $w = 1/\sigma^2(F)$; $\sigma(F)$ values were derived from the previously calculated $\sigma(I)$ values. $R$ at this point was 0.12 and a difference Fourier map revealed all the H atoms except those in the C(11) methyl group (see Fig. 1 for the crystallographic numbering scheme). H atoms were included in the refinement with isotropic temperature factors. Two further cycles gave a difference map showing the missing methyl H atoms. In the final stages of refinement, extinction effects were apparent in the data and a correction was applied. A parameter E was introduced such that $F_c$ was replaced in the calculations by $F_{corr}$, where $F_{corr} = F_c/(1 + EI_o)$, $I_o$ being the uncorrected intensity (Stout & Jensen, 1968). The final refined value of E was 1.8 (2) $\times$ 10$^{-7}$, and the correction produced a marked improvement in the agreement for strong, low-angle planes. Analysis of the weighting statistics showed 100 and $\overline{1}21$ to be so severely affec-

ted by extinction that the correction was insufficient to compensate for it; these planes were zero weighted in the final refinement cycles. Six other planes were assigned zero weight due to poor agreement revealed by analysis of the weighting statistics: $\bar{3}1\bar{4}$ (which had clearly been measured incorrectly and did not agree with the preliminary X-ray photographs), $\bar{2}\bar{8}3$, 210, 0,23,1, $\bar{4}25$ and 49$\bar{1}$. The final $R$ and $R'\{ = [\Sigma\ w(|F_o| - |F_c|)^2/\Sigma\ w|F_o|^2]^{1/2}\}$ for the 1362 reflexions with $I >$

$3\sigma(I)$ are 0·048 and 0·066 respectively. For all 1557 data (with no planes zero weighted) $R$ is 0·053 and $R'$ is 0·109.* The error in an observation of unit weight $\{[\Sigma\ w(|F_o| - |F_c|)^2/(m - n)]^{1/2}\}$ is 2·96. The largest change/error in the final cycle of refinement was 0·03.

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\* A list of structure factors for both compounds has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32152 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Final positional parameters for* (I) (*fractional*, $\times 10^4$, H $\times 10^3$) *with estimated standard deviations in parentheses*

| | $x$ | $y$ | $z$ |
|---|---|---|---|
| O(1) | 4693 (2) | 3686 (1) | −967 (2) |
| O(2) | 7695 (2) | 4697 (1) | 6205 (2) |
| C(1) | 5079 (3) | 4012 (1) | 512 (2) |
| C(2) | 6786 (3) | 4415 (1) | 924 (3) |
| C(3) | 7623 (3) | 4636 (1) | 2764 (3) |
| C(4) | 6936 (3) | 4473 (1) | 4538 (2) |
| C(5) | 5330 (3) | 4020 (1) | 4217 (2) |
| C(6) | 6134 (3) | 3375 (1) | 4769 (2) |
| C(7) | 4585 (3) | 2918 (1) | 3930 (3) |
| C(8) | 2879 (3) | 3029 (1) | 2626 (3) |
| C(9) | 2203 (3) | 3635 (1) | 1816 (3) |
| C(10) | 3927 (2) | 4058 (1) | 2037 (2) |
| C(11) | 7970 (3) | 3214 (1) | 4187 (4) |
| C(12) | 791 (4) | 3603 (2) | −323 (4) |
| H(2) | 725 (3) | 451 (1) | −23 (3) |
| H(3) | 873 (3) | 489 (1) | 306 (3) |
| H(5) | 459 (3) | 412 (1) | 511 (3) |
| H(6) | 646 (3) | 336 (1) | 617 (3) |
| H(7) | 493 (3) | 252 (1) | 430 (3) |
| H(8) | 196 (4) | 271 (1) | 215 (4) |
| H(9) | 150 (3) | 382 (1) | 274 (3) |
| H(10) | 347 (3) | 446 (1) | 184 (3) |
| H(11a) | 776 (3) | 322 (1) | 269 (4) |
| H(11b) | 906 (3) | 351 (1) | 484 (3) |
| H(11c) | 832 (4) | 281 (1) | 458 (4) |
| H(12a) | −43 (5) | 340 (1) | −26 (4) |
| H(12b) | 47 (4) | 403 (1) | −85 (4) |
| H(12c) | 144 (5) | 341 (1) | −120 (4) |

Table 2. *Final parameters for* (I) *and their estimated standard deviations*

(a) Anisotropic thermal parameters ($U_{ij} \times 10^3$ Å$^2$) in the expression:

$$f = f^0\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)].$$

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| O(1) | 106 (1) | 76 (1) | 46 (1) | −15 (1) | 33 (1) | −18 (1) |
| O(2) | 85 (1) | 68 (1) | 49 (1) | −14 (1) | 13 (1) | −16 (1) |
| C(1) | 69 (1) | 43 (1) | 35 (1) | 7 (1) | 16 (1) | 5 (1) |
| C(2) | 74 (1) | 56 (1) | 46 (1) | 0 (1) | 27 (1) | 9 (1) |
| C(3) | 70 (1) | 57 (1) | 55 (1) | −14 (1) | 22 (1) | 0 (1) |
| C(4) | 65 (1) | 46 (1) | 42 (1) | 1 (1) | 14 (1) | −5 (1) |
| C(5) | 58 (1) | 48 (1) | 33 (1) | 1 (1) | 19 (1) | −3 (1) |
| C(6) | 72 (1) | 55 (1) | 33 (1) | 5 (1) | 15 (1) | 8 (1) |
| C(7) | 93 (2) | 46 (1) | 60 (1) | −5 (1) | 25 (1) | 11 (1) |
| C(8) | 80 (1) | 67 (1) | 63 (1) | −23 (1) | 21 (1) | −1 (1) |
| C(9) | 57 (1) | 75 (1) | 52 (1) | −4 (1) | 18 (1) | −7 (1) |
| C(10) | 55 (1) | 44 (1) | 39 (1) | 7 (1) | 13 (1) | 1 (1) |
| C(11) | 78 (2) | 66 (1) | 66 (1) | 21 (1) | 21 (1) | 14 (1) |
| C(12) | 65 (1) | 112 (2) | 71 (2) | −7 (1) | 3 (1) | −5 (1) |

(b) Isotropic thermal parameters ($U \times 10^3$)

| | $U$ (Å$^2$) | | $U$ (Å$^2$) | | $U$ (Å$^2$) |
|---|---|---|---|---|---|
| H(2) | 65 (5) | H(8) | 94 (7) | H(11c) | 93 (7) |
| H(3) | 72 (6) | H(9) | 75 (6) | H(12a) | 113 (9) |
| H(5) | 51 (4) | H(10) | 60 (5) | H(12b) | 97 (8) |
| H(6) | 67 (6) | H(11a) | 78 (6) | H(12c) | 103 (9) |
| H(7) | 82 (7) | H(11b) | 77 (6) | | |
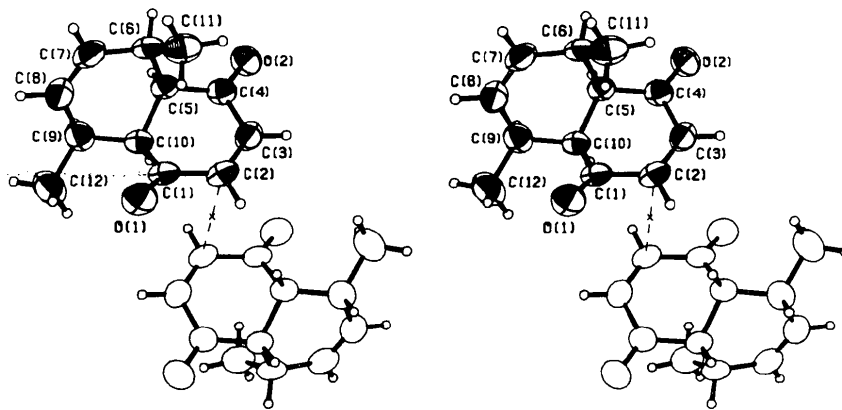


Fig. 1. Stereo diagram of 5$\alpha$,8$\alpha$-dimethyl-4a$\beta$,5,8,8a$\beta$-tetrahydro-1,4-naphthoquinone showing the crystallographic numbering scheme. H atoms are labelled according to the C atoms to which they are bonded. Non-hydrogen atoms are shown with 50% probability vibration ellipsoids, shaded for the asymmetric unit and open for the symmetry-related molecule. The centre of symmetry is indicated by the cross.

Table 3. *Final positional parameters for* (III) *(fractional,* $\times 10^4$, H $\times 10^3$) *with estimated standard deviations in parentheses*

The molecular centre of symmetry is at $(1,0,\frac{1}{2})$.

| | $x$ | $y$ | $z$ |
|---|---|---|---|
| O(1) | 7205 (1) | 243 (3) | 3992 (2) |
| O(2) | 9905 (2) | −882 (3) | 7968 (2) |
| C(1) | 7970 (2) | 378 (3) | 4779 (2) |
| C(2) | 9151 (2) | −414 (4) | 4594 (2) |
| C(3) | 9878 (2) | −851 (4) | 5780 (2) |
| C(4) | 9353 (2) | −536 (4) | 7036 (2) |
| C(5) | 8134 (2) | 187 (4) | 7078 (2) |
| C(6) | 7204 (2) | −1197 (4) | 7226 (2) |
| C(7) | 6002 (3) | −535 (5) | 6955 (3) |
| C(8) | 5764 (2) | 923 (5) | 6476 (3) |
| C(9) | 6672 (2) | 2198 (4) | 6166 (3) |
| C(10) | 7850 (2) | 1340 (3) | 5965 (2) |
| C(11) | 7417 (4) | −2779 (4) | 6472 (3) |
| C(12) | 6289 (3) | 3348 (5) | 5115 (3) |
| H(2) | 905 (2) | −133 (3) | 402 (2) |
| H(3) | 1011 (2) | −194 (3) | 576 (2) |
| H(5) | 813 (2) | 87 (3) | 780 (2) |
| H(6) | 726 (2) | −155 (3) | 812 (2) |
| H(7) | 537 (2) | −133 (3) | 711 (2) |
| H(8) | 495 (2) | 126 (3) | 631 (2) |
| H(9) | 678 (2) | 292 (4) | 689 (3) |
| H(10) | 844 (2) | 217 (3) | 599 (2) |
| H(11a) | 825 (3) | −332 (4) | 666 (3) |
| H(11b) | 732 (2) | −257 (3) | 560 (3) |
| H(11c) | 680 (3) | −361 (4) | 666 (3) |
| H(12a) | 689 (3) | 415 (4) | 488 (3) |
| H(12b) | 607 (3) | 272 (4) | 437 (3) |
| H(12c) | 563 (3) | 403 (5) | 539 (3) |

Table 4. *Final parameters for* (III) *and their estimated standard deviations*

(a) Anisotropic thermal parameters $(U_{ij} \times 10^3$ Å$^2)$

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| O(1) | 42 (1) | 74 (2) | 40 (1) | 8 (1) | −7 (1) | −13 (1) |
| O(2) | 51 (1) | 129 (2) | 44 (1) | 19 (1) | −3 (1) | 32 (1) |
| C(1) | 34 (1) | 41 (2) | 31 (1) | −2 (1) | 2 (1) | 0 (1) |
| C(2) | 37 (1) | 40 (2) | 33 (1) | 3 (1) | 1 (1) | −3 (1) |
| C(3) | 38 (2) | 40 (2) | 43 (2) | 7 (1) | 4 (1) | 9 (1) |
| C(4) | 37 (1) | 60 (2) | 39 (2) | 2 (1) | 1 (1) | 13 (1) |
| C(5) | 39 (1) | 49 (2) | 28 (1) | −2 (1) | 2 (1) | −4 (1) |
| C(6) | 50 (2) | 55 (2) | 33 (2) | −7 (2) | 5 (1) | 7 (1) |
| C(7) | 39 (2) | 72 (3) | 49 (2) | −16 (2) | 8 (1) | 0 (2) |
| C(8) | 31 (2) | 77 (3) | 47 (2) | 2 (2) | 5 (1) | −6 (2) |
| C(9) | 42 (2) | 51 (2) | 44 (2) | 8 (1) | 1 (1) | −12 (2) |
| C(10) | 29 (1) | 37 (2) | 36 (1) | −3 (1) | 1 (1) | −3 (1) |
| C(11) | 76 (3) | 47 (2) | 60 (2) | −9 (2) | 5 (2) | 5 (2) |
| C(12) | 62 (2) | 63 (3) | 63 (2) | 23 (2) | −1 (2) | 1 (2) |

(b) Isotropic thermal parameters $(U \times 10^3)$

| | $U$ (Å$^2$) | | $U$ (Å$^2$) | | $U$ (Å$^2$) |
|---|---|---|---|---|---|
| H(2) | 32 (6) | H(8) | 53 (8) | H(11c) | 85 (11) |
| H(3) | 30 (7) | H(9) | 51 (8) | H(12a) | 74 (11) |
| H(5) | 32 (6) | H(10) | 24 (6) | H(12b) | 83 (11) |
| H(6) | 43 (7) | H(11a) | 71 (10) | H(12c) | 88 (11) |
| H(7) | 51 (8) | H(11b) | 48 (8) | | |

The difference map showed random fluctuations with the highest peak at 0·23 e Å$^{-3}$. Atomic scattering factors for O and C atoms are those of Cromer & Mann (1968) and for H atoms those of Stewart, Davidson & Simpson (1965). Final positional and thermal parameters are listed in Tables 1 and 2.

*Photodimer* III

One hundred and eighty-nine $E$ values greater than 1·5 were derived as before, but a run of the automatic multisolution computer program did not produce any sets of phases with high consistency. Examination of a list of $\Sigma_2$ relationships showed the choice of starting symbols to be poor and the program was run again with a manually selected starting set. This run gave a good set of phases, and the $E$ map gave the positions of the non-hydrogen atoms. Refinement was carried out as before to $R = 0·11$, and the difference Fourier map showed the positions of all H atoms. Refinement continued as before and an extinction parameter was again necessary, the value of E refining to 5·1 (6) × $10^{-7}$. The weighting scheme used for (I) gave poor weight statistics for (III) and it was replaced by the following scheme: $\sqrt{w} = |F_o|/11·5$ for $|F_o| < 11·5$, and $\sqrt{w} = 11·5/|F_o|$ for $|F_o| \geq 11·5$. The final $R$ and $R'$ for the 1003 reflexions with $I > 3\sigma(I)$ are 0·050 and 0·046 respectively. For all 1458 data $R$ is 0·085 and $R'$ is 0·051.* The largest change/error in the final cycle of refinement was 0·31 and the highest difference-map peak was 0·21 e Å$^{-3}$. Scattering factors were as before. Final positional and thermal parameters are listed in Tables 3 and 4.

**Thermal-motion analysis**

The thermal motion has been analysed in terms of the rigid-body modes of translation, libration and screw motion (Schomaker & Trueblood, 1968) with the computer program *MGTLS*. For (I) the ten atoms in the ring system were taken to be a rigid body, giving a r.m.s. $\Delta U_{ij}$ value of 0·0021 Å$^2$, where $\Delta U_{ij} = U_{ij}$(observed) − $U_{ij}$(calculated from the rigid-body motion). The least-squares r.m.s. $\sigma(U_{ij})$ is 0·0010 Å$^2$. This suggests that the rigid body gives a good approximation to the thermal motion. Bond lengths in the rings have been corrected for libration (Cruickshank, 1956, 1961) with the shape parameter 0·08 for all atoms. Bonds outside the ten-atom core were further corrected for independent motion based on the $\Delta U_{ij}$ values (Busing & Levy, 1964; Johnson, 1970). A similar analysis was carried out for (III), except that the origin was fixed at the centre of symmetry and the screw tensor **S** set to zero. R.m.s. $\Delta U_{ij}$ for the ten-atom core was 0·0043 Å$^2$, compared to the least-squares r.m.s. $\sigma(U_{ij})$ of 0·0016 Å$^2$. Corrected bond lengths for both molecules are given in Table 5. The effects of the correction are reflected in the weighted mean C($sp^3$)—C($sp^3$) bond

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* See previous footnote.

distances for (I) and (III). These are 1·539 (6) and 1·539 (5) Å respectively before correction, and 1·544 (6) and 1·543 (6) Å after correction. Bond angles are not significantly affected and only uncorrected values are given in Table 6.

Table 5. *Bond lengths (Å) with estimated standard deviations in parentheses for non-hydrogen atoms*

|  | (I) | | (III) | |
|---|---|---|---|---|
|  | Uncorrected | Corrected | Uncorrected | Corrected |
| O(1)—C(1) | 1·211 (2) | 1·214 | 1·210 (3) | 1·210 |
| O(2)—C(4) | 1·222 (2) | 1·222 | 1·207 (3) | 1·208 |
| C(1)—C(2) | 1·481 (3) | 1·487 | 1·506 (4) | 1·507 |
| C(1)—C(10) | 1·509 (2) | 1·516 | 1·501 (3) | 1·505 |
| C(2)—C(3) | 1·327 (2) | 1·332 | 1·550 (4) | 1·555 |
| C(2)—C(3$^i$) | — | — | 1·559 (4) | 1·563 |
| C(3)—C(4) | 1·480 (2) | 1·486 | 1·510 (4) | 1·513 |
| C(4)—C(5) | 1·501 (2) | 1·508 | 1·507 (4) | 1·509 |
| C(5)—C(6) | 1·553 (2) | 1·562 | 1·546 (4) | 1·549 |
| C(5)—C(10) | 1·548 (2) | 1·554 | 1·544 (4) | 1·549 |
| C(6)—C(7) | 1·500 (3) | 1·503 | 1·492 (4) | 1·494 |
| C(7)—C(8) | 1·319 (3) | 1·325 | 1·306 (5) | 1·310 |
| C(8)—C(9) | 1·485 (3) | 1·492 | 1·497 (5) | 1·500 |
| C(9)—C(10) | 1·529 (3) | 1·537 | 1·527 (4) | 1·529 |
| C(6)—C(11) | 1·526 (3) | 1·533 | 1·530 (4) | 1·533 |
| C(9)—C(12) | 1·528 (3) | 1·532 | 1·519 (4) | 1·523 |

Symmetry code: (i) 2 − *x*, −*y*, 1 − *z*. (ii) 1 − *x*, 1 − *y*, −*z*.

Table 6. *Bond angles (°) with estimated standard deviations in parentheses for non-hydrogen atoms*

|  | (I) | (III) |
|---|---|---|
| O(1)—C(1)—C(2) | 120·0 (1) | 120·2 (2) |
| O(1)—C(1)—C(10) | 125·4 (2) | 124·6 (2) |
| C(2)—C(1)—C(10) | 114·5 (1) | 115·2 (2) |
| C(1)—C(2)—C(3) | 122·1 (1) | 116·9 (2) |
| C(1)—C(2)—C(3$^i$) | — | 113·5 (2) |
| C(3)—C(2)—C(3$^i$) | — | 89·4 (2) |
| C(2)—C(3)—C(4) | 121·4 (2) | 119·1 (2) |
| C(2)—C(3)—C(2$^i$) | — | 90·6 (2) |
| C(4)—C(3)—C(2$^i$) | — | 114·6 (2) |
| O(2)—C(4)—C(3) | 120·1 (2) | 119·9 (2) |
| O(2)—C(4)—C(5) | 122·2 (1) | 122·0 (3) |
| C(3)—C(4)—C(5) | 117·8 (1) | 118·1 (2) |
| C(4)—C(5)—C(6) | 111·6 (1) | 111·1 (2) |
| C(4)—C(5)—C(10) | 111·6 (1) | 112·8 (2) |
| C(6)—C(5)—C(10) | 112·3 (1) | 112·1 (2) |
| C(5)—C(6)—C(7) | 110·5 (2) | 110·6 (3) |
| C(5)—C(6)—C(11) | 116·2 (2) | 115·2 (2) |
| C(7)—C(6)—C(11) | 110·2 (2) | 110·3 (3) |
| C(6)—C(7)—C(8) | 125·4 (2) | 125·4 (3) |
| C(7)—C(8)—C(9) | 124·4 (2) | 124·2 (3) |
| C(8)—C(9)—C(10) | 110·6 (2) | 109·6 (3) |
| C(8)—C(9)—C(12) | 112·0 (2) | 113·1 (3) |
| C(10)—C(9)—C(12) | 114·9 (2) | 114·2 (2) |
| C(1)—C(10)—C(5) | 109·1 (1) | 109·3 (2) |
| C(1)—C(10)—C(9) | 118·6 (1) | 116·5 (2) |
| C(5)—C(10)—C(9) | 110·5 (1) | 109·4 (2) |

See Table 5 for symmetry code.

## Results and discussion

A stereo diagram of the molecule of (I), together with the centrosymmetrically related nearest neighbour, is shown in Fig. 1. The molecules are viewed for clarity in a direction 30° to the plane defined by C(1), C(2) and C(3). The corresponding view of the dimer III is shown in Fig. 2. The dimer is the result of C(2)—C(3$^{ii}$) and C(3)—C(2$^{ii}$) bonding under topochemical control. The geometrical relationship of the ene–dione systems is clearer in Fig. 3, where the view is perpendicular to the C(1),C(2),C(3) plane. The double bonds are offset with C(2) almost eclipsing C(2$^{ii}$). The intermolecular

contacts C(2)···C(2$^{ii}$) and C(2)···C(3$^{ii}$) are 3·624 and 4·040 Å respectively, the latter being equal to the separation of the mid-points of the double bonds. Equations of the mean planes of C(1),C(2),C(3),C(4) are given in Table 7, with deviations of atoms from the planes, for both (I) and (III). The four atoms deviate slightly, but significantly, from planarity in each case. The separation between neighbouring planes in (I) is 3·554 Å. While the orientation is not ideal for dimerization, the separation of the bond mid-points is just within the range 3·6–4·1 Å found to be photoactive for *trans*-cinnamic acids (Schmidt, 1964). Other members of the *cis*-4a,5,8,8a-tetrahydro-1,4-naphtho-
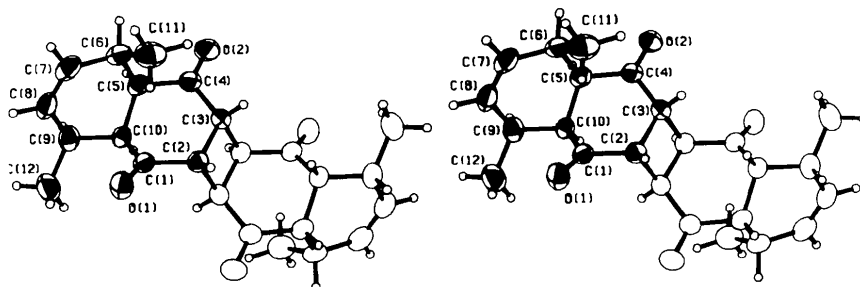


Fig. 2. Stereo diagram of the dimer in an orientation analogous to that of the monomer in Fig. 1.

quinone series with unfavourable C=C to C=C contacts undergo intramolecular reactions in the solid state (Dzakpasu, Phillips, Scheffer & Trotter, 1976).

Bond lengths and angles in the two molecules (see Tables 5 and 6) are normal. Bonds involving C(2) and C(3) undergo changes in length consistent with the change from $sp^2$ to $sp^3$ hybridization. The only other significant change in bond length is for O(2)—C(4), which is rather longer than O(1)—C(1) in (I), but is shortened to the same value in (III). The largest change in bond angle is 5·2° for C(1)—C(2)—C(3).

All six-membered rings have the half-chair conformation expected for cyclohexene on the basis of minimum-energy calculations (Bucourt & Hainaut, 1965), and torsion angles in the rings agree qualitatively with calculated values. The torsion angles (Table 8) are changed very little by dimerization. The r.m.s. change in ene–dione ring torsion angles is only 4·6, and 1·9° in the other ring. The degree of 'twist' about the
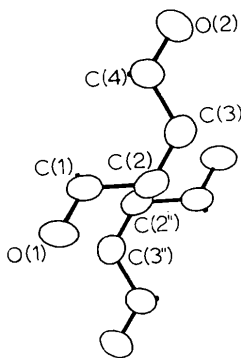


Fig. 3. Neighbouring ene–dione systems of monomer pairs viewed perpendicular to the plane of C(1),C(2),C(3). See Table 5 for the symmetry code.

C(5)—C(10) bond, as shown by the torsion angle C(6)—C(5)—C(10)—C(1), is increased in the dimer compared to the monomer. The angle is −72·8° in (I), larger than that found in any of the other 1,4-naphthoquinones of this type studied so far, presumably due to steric hindrance introduced by the C(11) methyl group. The largest value previously observed was −71·4° for

Table 8. *Torsion angles* (°) *with estimated standard deviations in parentheses*

A positive angle corresponds to a clockwise rotation of the nearest to eclipse the furthest bond.

|  | (I) | (III) |
|---|---|---|
| C(10)—C(1)—C(2)—C(3) | 22·0 (2) | 26·6 (2) |
| C(1)—C(2)—C(3)—C(4) | 2·4 (2) | 2·6 (3) |
| C(2)—C(3)—C(4)—C(5) | 3·4 (2) | 0·3 (3) |
| C(3)—C(4)—C(5)—C(10) | −31·9 (2) | −31·0 (3) |
| C(4)—C(5)—C(10)—C(1) | 53·4 (2) | 58·8 (2) |
| C(5)—C(10)—C(1)—C(2) | −48·9 (2) | −56·9 (2) |
| C(10)—C(5)—C(6)—C(7) | −38·7 (2) | −38·8 (3) |
| C(5)—C(6)—C(7)—C(8) | 10·5 (2) | 9·9 (3) |
| C(6)—C(7)—C(8)—C(9) | −1·6 (3) | −2·5 (4) |
| C(7)—C(8)—C(9)—C(10) | 20·8 (2) | 23·7 (3) |
| C(8)—C(9)—C(10)—C(5) | −48·0 (2) | −51·0 (2) |
| C(9)—C(10)—C(5)—C(6) | 59·3 (2) | 61·1 (2) |
| C(2)—C(1)—C(10)—C(9) | −176·5 (1) | 178·4 (2) |
| C(3)—C(4)—C(5)—C(6) | 94·7 (2) | 95·9 (2) |
| C(6)—C(5)—C(10)—C(1) | −72·8 (1) | −67·6 (2) |
| C(4)—C(5)—C(6)—C(7) | −164·9 (1) | −166·0 (2) |
| C(8)—C(9)—C(10)—C(1) | 78·9 (2) | 73·6 (2) |
| H(5)—C(5)—C(10)—H(10) | 61 (2) | 58 (2) |

Table 7. *Mean planes for the* C(1)—C(4) *group in the molecules*

Equations of the planes referred to an orthogonal system of axes parallel to the crystallographic *a*, *b*, and *c\** axes

(I)   $-0·5842x + 0·7897y - 0·1874z - 4·9049 = 0$
(III) $-0·4166x - 0·9091y - 0·0070z + 4·0508 = 0$

Deviations from the planes (Å)

|  | (I) | (III) |
|---|---|---|
| C(1) | 0·004 (2) | 0·005 (3) |
| C(2) | −0·010 (2) | −0·012 (3) |
| C(3) | 0·011 (2) | 0·013 (3) |
| C(4) | −0·004 (2) | −0·007 (3) |
| C(2$^{ii}$ or 2$^i$)† | 3·574 (2) | 1·397 (3) |
| C(3$^{ii}$ or 3$^i$)† | 3·532 (2) | 1·372 (3) |
| H(2)† | −0·03 (2) | −0·73 (2) |
| H(3)† | −0·01 (2) | −0·67 (3) |

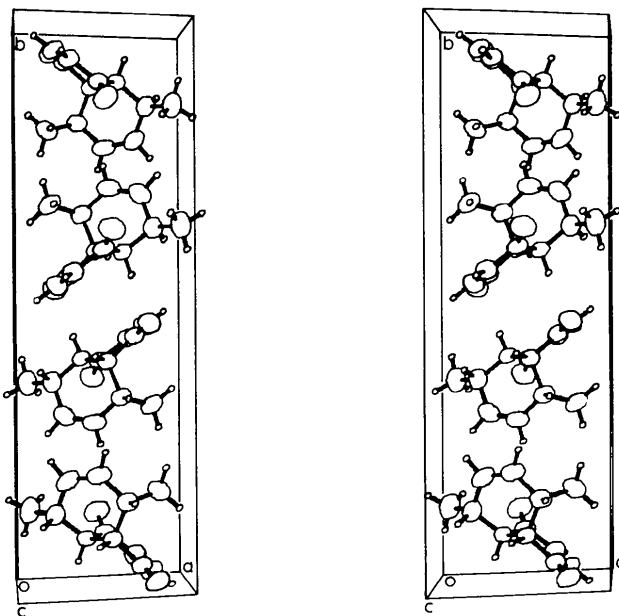† Atoms not included in the least-squares plane calculation. For symmetry code see Table 5.



Fig. 4. Stereo diagram of the contents of the unit cell for 5α,8α-dimethyl-4aβ,5,8,8aβ-tetrahydro-1,4-naphthoquinone viewed down *c*.
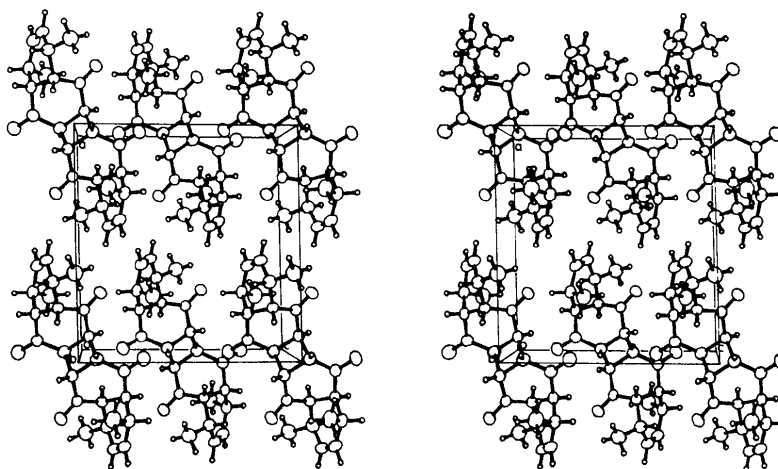
Fig. 5. Stereo diagram of the contents of the unit cell for the dimer viewed down b.

the 2,3,6,7-tetramethyl derivative (Phillips & Trotter, 1976).

The four-membered ring in (III) is constrained to be planar by the centre of symmetry, while cyclobutane itself has a puckered ring in the gas phase (Almenningen, Bastiansen & Skancke, 1961). Many structure determinations of molecules containing cyclobutane rings have been reported, and it appears that where the ring can have a centre of symmetry, it frequently crystallizes at a crystallographic centre. In other cases the ring tends to be puckered. For example, trans-1,3-cyclobutanedicarboxylic acid has a centrosymmetric, planar ring (Margulis & Fischer, 1967), while the cis isomer has a puckered ring with a torsion angle of 149° (Adman & Margulis, 1969). Ring bond lengths in the centrosymmetric case are 1·567 (6) and 1·552 (6) Å, agreeing well with those observed in (III). The weighted mean H—C($sp^3$) and H—C($sp^2$) distances are 0·98 (1) and 0·96 (1) Å for (I), and 0·97 (1) and 0·98 (2) Å for (III).

The packing of the molecules in the two structures is shown in Figs. 4 and 5. Pairs of molecules of (I) lie across centres of symmetry ($\frac{1}{2},\frac{1}{2},0$), and all other intermolecular contacts correspond to normal van der Waals interactions. Molecules of (III) lie on centres of symmetry (1,0,$\frac{1}{2}$), and the packing shows no strong intermolecular interactions. The two structures are related in that some short intermolecular contacts are common to both. Photolysis of (I), however, disrupts the lattice and single crystals of (III) can be obtained only by recrystallization.

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