Fig. 2. Stereo diagram of the contents of the unit cell projected down the *b* axis.

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2,3,4aβ,5β,8β,8aβ-Hexamethyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone

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Abstract. $C_{16}H_{22}O_2$, monoclinic, $C2/c$; $a=24\cdot930$ (7), $b=7\cdot795$ (3), $c=14\cdot472$ (5) Å, $\beta=101\cdot13$ (3)°; $d_m=1\cdot18$ (flotation), $d_x=1\cdot186$ g cm^{-3}, $Z=8$; μ(Cu $K\alpha)=6\cdot1$ cm^{-1}. The conformation of the molecule is twisted such that the bridgehead methyl groups are staggered with a torsion angle of $62\cdot6°$. Bond lengths and angles are close to normal values.

Introduction. Large, yellowish, rod-shaped crystals were obtained by crystallization from petroleum spirit. All the crystals examined proved to be twinned and a sample suitable for data collection was obtained by splitting a large crystal such that only a small amount of one twin remained. Unit-cell and intensity data were measured on a Datex-automated G.E. XRD 6 dif-

fractometer with Cu $K\alpha$ radiation and the θ–2θ scan technique. Unit-cell parameters were refined by least squares from the observed 2θ values of 16 reflexions. Of the 2051 independent reflexions with $2\theta<120°$, 1661 had intensities greater than $3\sigma(I)$ above background $[\sigma^2(I)=S+B+(0\cdot04S)^2$, where $S=$ scan and $B=$ background count]. Lorentz and polarization corrections were applied and the structure amplitudes derived. Crystal dimensions were approximately $0\cdot03\times0\cdot03\times0\cdot07$ cm and no absorption correction was applied.

Attempts to solve the structure in $C2/c$ with an automatic computer program utilizing multisolution direct methods (Long, 1965) were unsuccessful. The solution was obtained in Cc from manually-selected starting reflexions in a symbolic addition and tangent

refinement procedure. The space group proved to be $C2/c$ as predicted from the E statistics. The cause of the problem was the failure of the high probability Σ_1 relationship between $E(600) = 2\cdot63$ and $E(12,0,0) = 3\cdot87$, the correct phase of $12,0,0$ being π rather than the predicted value of 0. Selecting the starting reflexions so that this relationship was not used early in the sign-determination procedure allowed the correct assignments to be made. The correct set yielded an E map in which all the non-hydrogen atoms were located. Several cycles of full-matrix least squares were carried out where the function minimized was $\sum w(|F_o| - |F_c|)^2$ with weights $w = 1/\sigma^2(F)$, $\sigma(F)$ values being derived from the previously calculated $\sigma(I)$ values. A difference Fourier map revealed the positions of all but five of the hydrogen atoms. The remaining hydrogens were located on a subsequent difference map. All non-hydrogen atoms were included with anisotropic temperature factors, the hydrogens being refined isotropically. The final R and R' $\{ = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}\}$ for the 1661 reflexions with $I > 3\sigma(I)$ are $0\cdot070$ and $0\cdot093$

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

	x	y	z
O(1)	2930 (1)	273 (4)	3184 (2)
O(2)	3941 (1)	5982 (4)	4424 (2)
C(1)	3172 (1)	1556 (4)	3504 (2)
C(2)	2856 (1)	3064 (4)	3730 (2)
C(3)	3098 (1)	4561 (5)	3982 (2)
C(4)	3700 (1)	4763 (4)	4013 (2)
C(5)	3989 (1)	3434 (4)	3506 (2)
C(6)	3794 (1)	3730 (4)	2420 (2)
C(7)	3933 (1)	2191 (5)	1877 (2)
C(8)	4038 (1)	655 (5)	2230 (2)
C(9)	4035 (1)	175 (4)	3221 (2)
C(10)	3803 (1)	1613 (4)	3763 (2)
C(11)	2254 (2)	2745 (8)	3670 (4)
C(12)	2811 (2)	6122 (8)	4248 (5)
C(13)	4611 (1)	3699 (6)	3786 (3)
C(14)	4010 (2)	5366 (6)	2054 (3)
C(15)	4599 (2)	−573 (6)	3695 (3)
C(16)	3931 (2)	1281 (6)	4834 (2)
H(6)	340 (2)	388 (5)	235 (3)
H(7)	396 (2)	237 (5)	124 (3)
H(8)	411 (1)	−31 (5)	186 (3)
H(9)	376 (1)	−89 (4)	321 (2)
H(11a)	221 (2)	184 (7)	396 (4)
H(11b)	207 (2)	381 (7)	372 (4)
H(11c)	211 (3)	250 (8)	302 (6)
H(12a)	278 (3)	682 (9)	385 (6)
H(12b)	310 (3)	713 (11)	462 (6)
H(12c)	260 (2)	591 (8)	463 (4)
H(13a)	469 (1)	492 (5)	374 (2)
H(13b)	480 (1)	304 (4)	336 (3)
H(13c)	476 (2)	330 (5)	444 (3)
H(14a)	391 (2)	642 (5)	235 (3)
H(14b)	385 (2)	550 (5)	127 (3)
H(14c)	438 (3)	536 (7)	201 (4)
H(15a)	470 (2)	−146 (6)	336 (3)
H(15b)	461 (2)	−107 (5)	431 (3)
H(15c)	489 (2)	36 (6)	387 (3)
H(16a)	380 (1)	10 (5)	490 (2)
H(16b)	373 (2)	212 (6)	519 (3)
H(16c)	432 (2)	123 (6)	509 (3)

respectively. For all 2051 data R is $0\cdot083$ and R' is $0\cdot094$. The error in an observation of unit weight, $[\sum w(|F_o| - |F_c|)^2/(m-n)]^{1/2}$, is $2\cdot54$. Atomic scattering factors for O and C are those of Cromer & Mann (1968) and for H those of Stewart, Davidson & Simpson (1965). Final positional and thermal parameters are listed in Tables 1 and 2.*

Table 2. *Final thermal parameters and their estimated standard deviations*

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

(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)	40 (1)	68 (2)	91 (2)	−11 (1)	8 (1)	−19 (1)
O(2)	68 (2)	67 (2)	84 (2)	−14 (1)	23 (1)	−30 (2)
C(1)	30 (2)	55 (2)	38 (2)	−1 (1)	2 (1)	1 (1)
C(2)	33 (2)	63 (2)	40 (2)	6 (2)	12 (1)	10 (2)
C(3)	45 (2)	59 (2)	44 (2)	9 (2)	19 (2)	2 (2)
C(4)	49 (2)	47 (2)	42 (2)	−1 (2)	12 (1)	−1 (2)
C(5)	30 (2)	52 (2)	35 (2)	−3 (1)	5 (1)	−1 (1)
C(6)	36 (2)	56 (2)	39 (2)	6 (2)	10 (1)	8 (2)
C(7)	51 (2)	73 (3)	33 (2)	4 (2)	11 (1)	−4 (2)
C(8)	47 (2)	61 (2)	44 (2)	5 (2)	9 (2)	−9 (2)
C(9)	35 (2)	51 (2)	43 (2)	4 (2)	5 (1)	0 (2)
C(10)	28 (2)	50 (2)	34 (2)	1 (1)	3 (1)	0 (1)
C(11)	37 (2)	97 (4)	81 (3)	7 (2)	21 (2)	21 (3)
C(12)	81 (3)	72 (3)	103 (4)	22 (3)	44 (3)	−4 (3)
C(13)	33 (2)	69 (3)	59 (2)	−9 (2)	6 (2)	2 (2)
C(14)	61 (3)	69 (3)	66 (3)	5 (2)	25 (2)	14 (2)
C(15)	46 (2)	63 (3)	65 (3)	18 (2)	6 (2)	2 (2)
C(16)	47 (2)	68 (3)	33 (2)	2 (1)	3 (1)	6 (2)

(b) Isotropic thermal parameters ($U_{iso} \times 10^2$ Å^2)

	U		U		U
H(6)	7 (1)	H(7)	7 (1)	H(8)	6 (1)
H(9)	5 (1)	H(11a)	11 (2)	H(11b)	12 (2)
H(11c)	15 (3)	H(12a)	16 (3)	H(12b)	18 (3)
H(12c)	12 (2)	H(13a)	5 (1)	H(13b)	5 (1)
H(13c)	8 (1)	H(14a)	7 (1)	H(14b)	8 (1)
H(14c)	12 (2)	H(15a)	8 (1)	H(15b)	7 (1)
H(15c)	8 (1)	H(16a)	6 (1)	H(16b)	9 (1)
H(16c)	10 (2)				

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*. The ten atoms in the ring system were taken to be a rigid body giving an r.m.s. ΔU_{ij} value of $0\cdot0016$ Å^2 compared to the least-squares r.m.s. $\sigma(U_{ij})$ of $0\cdot0021$ Å^2. Bond lengths in the rings have been corrected for libration (Cruickshank, 1956, 1961) with the shape parameter $0\cdot08$ for all atoms. Bonds outside the ten-atom core were further corrected for independent motion based on the ΔU_{ij} values (Busing & Levy, 1964; Johnson, 1970).

Corrected bond lengths are shown in Table 3. Corrections to bond angles are not significant and are not reported.

Table 3. *Bond lengths* (Å) *for non-hydrogen atoms with estimated standard deviations in parentheses*

		Corrected			Corrected
O(1)—C(1)	1·213 (4)	1·216	O(2)–C(4)	1·216 (4)	1·216
C(1)—C(2)	1·485 (5)	1·489	C(1)–C(10)	1·546 (4)	1·551
C(2)—C(3)	1·331 (5)	1·336	C(3)–C(4)	1·503 (5)	1·507
C(4)—C(5)	1·527 (4)	1·532	C(5)–C(6)	1·570 (4)	1·575
C(5)—C(10)	1·560 (4)	1·565	C(6)–C(7)	1·509 (5)	1·514
C(7)—C(8)	1·309 (5)	1·312	C(8)–C(9)	1·484 (5)	1·488
C(9)—C(10)	1·544 (5)	1·549	C(2)–C(11)	1·509 (5)	1·512
C(3)—C(12)	1·499 (6)	1·502	C(5)–C(13)	1·540 (4)	1·543
C(6)—C(14)	1·519 (5)	1·521	C(9)–C(15)	1·553 (5)	1·555
C(10)–C(16)	1·542 (4)	1·545			

Discussion. The structural work on 2,3,4aβ,5β,8β,8aβ-hexamethyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (I) was undertaken as part of a study of the photochemistry of various substituted 1,4-naphthoquinone systems with *cis* bridgehead substituents.

(I)   (II)
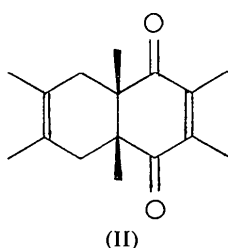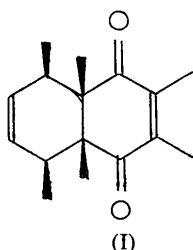
A stereo diagram of the molecule, with the crystallographic numbering scheme, is shown in Fig. 1. The conformation is seen to be staggered about the C(5)–C(10) bond as in *cis*-2,3,4a,6,7,8a-hexamethyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (II) (Phillips & Trotter, 1976). The degree of 'twist' about this central bond
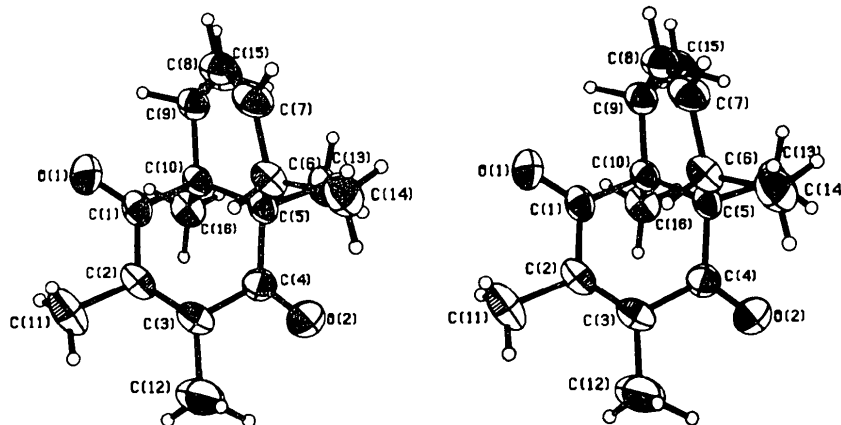
is shown by the torsion angles C(6)–C(5)–C(10)–C(1) and C(13)–C(5)–C(10)–C(16) of −60·7 (3) and 62·6 (3)° respectively compared to −61·4 (5) and 60·0 (6)° for (II). This increase in twist for (I) as compared to (II) is the result of steric hindrance between the bridgehead, and C(14) and C(15) methyl groups. In (II) the latter are bonded to C(7) and C(8) and are out of range of the bridgehead substituents. The result of this effect is to bring H(6) closer to the C=C double bond such that C(2)···H(6) and C(3)···H(6) are 2·70 (3) and 2·66 (3) Å respectively, 0·19 and 0·14 Å shorter than the corresponding distances in (II). This would appear to favour the process of hydrogen abstraction by enone carbon.

A further effect of the methyl group interactions is to change the torsion angle H(9)–C(9)–C(10)–C(1) from its value of −42 (3)° in (II) to −37 (2)° in (I). This reduces the O(1)···H(9) distance by 0·21 Å to 2·26 (3) Å thus facilitating the β-hydrogen abstraction process. The result is that the photolysis of (I) in solution gives products corresponding to those observed for (II) in a similar ratio (Scheffer, Jennings & Louwerens, 1976). The same products result from the solid-state photolysis of (I) (Scheffer & Dzakpasu, 1975).

The bond lengths and angles in the molecule (see Tables 3 and 4) are largely normal with equivalent C=O distances. The main differences from (II) consist of lengthening of the C(5)–C(6) and C(5)–C(10) bonds and a corresponding shortening of the C(6)–C(7), C(7)–C(8) and C(8)–C(9) bonds, as a result of the methyl group interactions. Changes in the bond angles may also be attributed to this effect. As in (II) there are interactions between the carbonyl oxygen atoms and neighbouring methyl groups, O(1)···H(11a) and O(2)···H(12b) being 2·61 (3) and 2·35 (3) Å respectively.

A stereo diagram of the packing arrangement in the unit cell is shown in Fig. 2. Intermolecular distances correspond to van der Waals contacts and no strong intermolecular interactions are apparent.
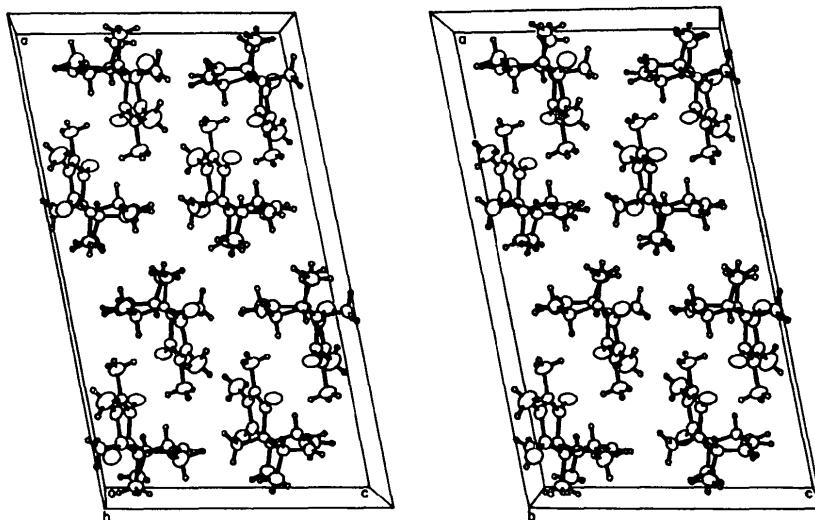

Fig. 1. Stereo diagram of 2,3,4aβ,5β,8β,8aβ-hexamethyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone.

Fig. 2. Stereo diagram of the contents of the unit cell projected down the *b* axis.

Table 4. *Bond angles* (°) *for non-hydrogen atoms with estimated standard deviations in parentheses*

O(1)—C(1)—C(2)	119·5 (3)	O(1)-C(1)—C(10)	121·5 (3)
C(2)—C(1)—C(10)	118·7 (3)	C(1)-C(2)—C(3)	121·6 (3)
C(2)—C(3)—C(4)	119·7 (3)	O(2)-C(4)—C(3)	119·5 (3)
O(2)—C(4)—C(5)	122·1 (3)	C(3)-C(4)—C(5)	118·4 (3)
C(4)—C(5)—C(6)	107·3 (2)	C(4)-C(5)—C(10)	108·3 (2)
C(6)—C(5)—C(10)	108·9 (2)	C(5)-C(6)—C(7)	110·3 (3)
C(6)—C(7)—C(8)	125·0 (3)	C(7)-C(8)—C(9)	124·7 (3)
C(8)—C(9)—C(10)	112·4 (3)	C(1)-C(10)-C(5)	107·7 (2)
C(1)—C(10)-C(9)	108·7 (2)	C(5)-C(10)-C(9)	112·4 (2)
C(1)—C(2)—C(11)	114·9 (4)	C(3)-C(2)—C(11)	123·5 (4)
C(2)—C(3)—C(12)	124·7 (4)	C(4)-C(3)—C(12)	115·5 (4)
C(4)—C(5)—C(13)	109·1 (3)	C(6)-C(5)—C(13)	110·2 (3)
C(10)-C(5)—C(13)	113·0 (3)	C(5)-C(6)—C(14)	114·2 (3)
C(7)—C(6)—C(14)	110·7 (3)	C(8)-C(9)—C(15)	110·4 (3)
C(10)-C(9)—C(15)	116·4 (3)	C(1)-C(10)-C(16)	104·0 (3)
C(5)—C(10)-C(16)	112·3 (3)	C(9)-C(10)-C(16)	111·1 (3)

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