à 2,186 Å (valeur moyenne: 2,178 Å) et les distances S–S de 3,531 à 3,575 (valeur moyenne: 3,556 Å). Ces résultats infirment la conclusion de Schäfer *et al.* (1964), qui ayant trouvé des distances Mo–S variant de 2,21 à 2,15 Å et des distances S–S variant de 3,46 à 3,61 Å, en avaient déduit que le tétraèdre MoS_4 était peu régulier.

Tableau 2. *Environnement du molybdène*

Les distances sont exprimées en Å, les angles en degrés décimaux, les écarts types portant sur la dernière décimale sont indiqués entre parenthèses. L'atome S′(1) se déduit de S(1) par l'opération de symétrie: $x, \frac{1}{2}-y, z$.

Distances

Mo–S(1)	2,177 (5)	S(1)–S′(1)	3,531 (10)
Mo–S′(1)	2,177 (5)	S(1)–S(3)	3,543 (6)
Mo–S(2)	2,171 (5)	S(1)–S(4)	3,572 (6)
Mo–S(3)	2,186 (6)	S′(1)–S(3)	3,543 (6)
		S′(1)–S(4)	3,572 (6)
		S(3)–S(4)	3,575 (8)

Angles de valence

S(1)–Mo–S′(1)	108,40 (15)
S(1)–Mo–S(2)	109,15 (15)
S(1)–Mo–S(3)	109,91 (15)
S′(1)–Mo–S(2)	109,15 (15)
S′(1)–Mo–S(3)	109,91 (15)
S(2)–Mo–S(3)	110,29 (20)

Tableau 3. *Distances molybdène–azote*

Les distances sont exprimées en Å, les écarts types portant sur la dernière décimale sont indiqués entre parenthèses; les atomes d'azote se déduisent de ceux donnés dans le Tableau 1 par les opérations de symétrie suivantes:

i	x	y	z	v	$x-\frac{1}{2}$	y	$\frac{1}{2}-z$
ii	$x-1$	y	z	vi	$\frac{1}{2}-x$	$-y$	$z-\frac{1}{2}$
iii	$1-x$	$-y$	$-z$	vii	$\frac{1}{2}-x$	$1-y$	$z-\frac{1}{2}$
iv	$1-x$	$1-y$	$-z$				

Mo–N(1^{i})	3,950 (18)	Mo–N(2^{v})	4,046 (18)
Mo–N(1^{ii})	3,990 (17)	Mo–N(2^{vi})	4,172 (11)
Mo–N(1^{iii})	4,215 (10)	Mo–N(2^{vii})	4,172 (11)
Mo–N(1^{iv})	4,215 (10)		

Les distances entre le molybdène et les atomes d'azote les plus proches sont données dans le Tableau 3.

Nous remercions les membres du laboratoire de cristallographie de Montpellier pour les possibilités de mesure qu'ils nous ont offertes. Nous remercions également la direction de l'O.C.M. à Abidjan qui nous a permis d'effectuer les calculs sur ses ordinateurs 370-145.

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cis-2,3,4a,6,7,8a-Hexamethyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone

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Abstract. $C_{16}H_{22}O_2$, monoclinic, $P2_1/c$; $a=7{\cdot}312$ (3), $b=11{\cdot}540$ (4), $c=16{\cdot}674$ (3) Å, $\beta=92{\cdot}26$ (3)°; $d_m=1{\cdot}16$ (flotation), $d_x=1{\cdot}163$ g cm^{-3}, $Z=4$; μ(Cu $K\alpha$)$=6{\cdot}0$ cm^{-1}. The conformation of the molecule is twisted such that the bridgehead methyl groups are staggered with a torsion angle of 60·0°. Bond lengths and angles are close to normal values.

Introduction. Small, colourless, well formed crystals were obtained by slow crystallization from acetone. Unit-cell and intensity data were measured on a Datex-automated G.E. XRD 6 diffractometer 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 15 reflexions. Of the 2786 independent reflexions with $2\theta<145°$, 1385 had intensities greater than $3\sigma(I)$ above background [$\sigma^2(I)=S+B+(0{\cdot}04S)^2$, where S=scan and B=background count]. Lorentz and polarization corrections were applied and the structure amplitudes derived. Crystal dimensions were $0{\cdot}015\times0{\cdot}020\times0{\cdot}020$ cm and no absorption correction was applied.

The structure was solved by direct methods with the multisolution procedure (Long, 1965). Complications arose as a result of the pseudo C-centring of the lattice and only five of the 326 E values greater than 1·5 had indices with $h+k$ odd. Several of the most probable E maps were examined and all contained multiple images of the molecule and a pseudo twofold axis. The correct position of the molecule was found to be the average of the two images in one of the E maps. This located the molecule such that its approximate twofold axis coincided with the crystallographic pseudo twofold axis. All the non-hydrogen atoms were found in this way and were refined by the full-matrix least-squares procedure where the function minimized

was $\sum w(|F_o|-|F_c|)^2$ with weights $w=1/\sigma^2(F)$, where $\sigma(F)$ values were derived from the previously calculated $\sigma(I)$ values. A difference map showed the positions of most of the hydrogen atoms and the presence of a disordered molecule related to the first by the pseudo twofold axis at $(\frac{1}{4},y,\frac{1}{4})$. The only atomic positions which are not approximately superimposed for the two molecules are those for substituents on C(1), C(4), C(6) and C(9) (see Fig. 1 for crystallographic numbering scheme). The relative occupancies were estimated from the peak heights corresponding to O(1) and O(2) for both molecules in a Fourier map phased from the C atom positions alone. O(1), O(2), H(6*a*), H(6*b*), H(9*a*) and H(9*b*) were included in the subsequent refinement with occupancy 0·824 and the related oxygen atoms [*O(1) and *O(2)] were also refined with occupancy 0·176. All non-hydrogen atoms, except *O(1) and *O(2), were included with anisotropic temperature factors, *O(1), *O(2) and the H atoms being refined isotropically. 17 planes were given zero weight in the final stages of refinement due to poor agreement, probably resulting from imperfect treatment of the disorder. The final R and R' $\{=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}\}$ for the 1385 reflexions with $I>3\sigma(I)$ are 0·088 and 0·120 respectively. For all 2786 data R is 0·177 and R' is 0·122. The error in an observation of unit weight, $[\sum w(|F_o|-|F_c|)^2/(m-n)]^{1/2}$, is 2·56. 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 1. *Final positional parameters (fractional* $\times 10^4$, *O(1), *O(2) *and* H $\times 10^3$) *with estimated standard deviations in parentheses*

	x	*y*	*z*
O(1)	−271 (6)	1263 (4)	1834 (3)
O(2)	5966 (6)	3544 (5)	1890 (3)
C(1)	1142 (7)	1843 (5)	1819 (3)
C(2)	2542 (7)	1583 (5)	1217 (3)
C(3)	4186 (8)	2094 (5)	1276 (3)
C(4)	4680 (7)	2925 (5)	1930 (3)
C(5)	3435 (7)	2970 (5)	2636 (3)
C(6)	3827 (8)	1909 (6)	3162 (4)
C(7)	2382 (9)	1655 (5)	3769 (3)
C(8)	724 (7)	2116 (5)	3721 (3)
C(9)	162 (9)	2929 (7)	3048 (4)
C(10)	1413 (6)	2947 (5)	2326 (3)
C(11)	2073 (13)	737 (7)	563 (4)
C(12)	5698 (11)	1896 (9)	714 (5)
C(13)	3916 (11)	4067 (8)	3134 (5)
C(14)	3132 (11)	785 (7)	4395 (5)
C(15)	−727 (10)	1877 (7)	4332 (5)
C(16)	904 (11)	3978 (6)	1782 (4)
H(6*a*)	409 (13)	109 (8)	280 (5)
H(6*b*)	515 (7)	192 (4)	345 (3)
H(9*a*)	8 (7)	385 (5)	330 (3)
H(9*b*)	−117 (8)	263 (5)	289 (3)
H(11*a*)	62 (8)	60 (5)	69 (3)
H(11*b*)	256 (8)	104 (6)	3 (4)
H(11*c*)	274 (7)	−4 (5)	59 (3)
H(12*a*)	596 (9)	101 (6)	63 (4)
H(12*b*)	533 (8)	169 (5)	15 (4)
H(12*c*)	610 (8)	262 (5)	49 (4)
H(13*a*)	419 (8)	485 (6)	290 (4)
H(13*b*)	323 (6)	418 (4)	362 (3)
H(13*c*)	489 (10)	386 (7)	355 (5)
H(14*a*)	388 (7)	119 (5)	487 (3)
H(14*b*)	199 (9)	58 (5)	473 (4)
H(14*c*)	354 (6)	4 (4)	422 (3)
H(15*a*)	−200 (8)	141 (5)	403 (3)
H(15*b*)	−24 (12)	224 (8)	481 (5)
H(15*c*)	−182 (14)	275 (10)	421 (6)
H(16*a*)	155 (9)	472 (6)	204 (4)
H(16*b*)	185 (8)	377 (6)	125 (4)
H(16*c*)	−48 (8)	410 (6)	181 (4)
*O(1)	515 (5)	126 (4)	310 (3)
*O(2)	−112 (5)	357 (3)	305 (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)

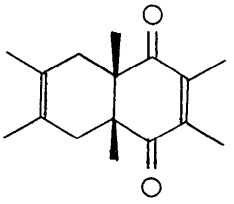
	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	57 (3)	67 (3)	63 (3)	−26 (3)	−3 (2)	5 (3)
O(2)	51 (3)	99 (4)	80 (4)	−37 (3)	23 (2)	−2 (3)
C(1)	47 (3)	49 (4)	46 (4)	7 (3)	−14 (2)	0 (3)
C(2)	51 (3)	48 (4)	41 (3)	−3 (3)	3 (2)	5 (3)
C(3)	79 (4)	56 (4)	24 (4)	16 (3)	25 (2)	2 (3)
C(4)	47 (3)	60 (4)	48 (4)	−12 (3)	12 (2)	20 (3)
C(5)	61 (3)	49 (4)	35 (3)	1 (3)	9 (2)	−4 (3)
C(6)	52 (3)	64 (5)	46 (4)	16 (3)	11 (3)	−4 (3)
C(7)	89 (4)	52 (4)	35 (3)	−19 (3)	−2 (3)	−2 (3)
C(8)	41 (3)	58 (4)	63 (4)	−4 (3)	−5 (3)	−9 (4)
C(9)	64 (4)	71 (5)	54 (4)	−8 (4)	2 (3)	15 (4)
C(10)	35 (3)	52 (4)	51 (4)	11 (3)	0 (2)	1 (3)
C(11)	111 (6)	72 (6)	43 (4)	0 (5)	8 (4)	−5 (4)
C(12)	99 (6)	86 (7)	59 (5)	22 (5)	26 (4)	0 (5)
C(13)	90 (5)	80 (6)	56 (4)	−20 (5)	6 (4)	−25 (4)
C(14)	90 (5)	63 (5)	52 (4)	−2 (4)	−2 (4)	18 (4)
C(15)	74 (4)	99 (6)	57 (4)	−13 (5)	40 (4)	−7 (4)
C(16)	93 (5)	44 (4)	60 (4)	18 (4)	5 (4)	−2 (3)

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

	U		*U*		*U*
H(6*a*)	11 (3)	H(6*b*)	2 (1)	H(9*a*)	3 (1)
H(9*b*)	5 (2)	H(11*a*)	9 (2)	H(11*b*)	11 (2)
H(11*c*)	7 (2)	H(12*a*)	11 (2)	H(12*b*)	8 (2)
H(12*c*)	8 (2)	H(13*a*)	9 (2)	H(13*b*)	11 (2)
H(13*c*)	4 (1)	H(14*a*)	8 (2)	H(14*b*)	11 (2)
H(14*c*)	4 (1)	H(15*a*)	9 (2)	H(15*b*)	18 (4)
H(15*c*)	24 (5)	H(16*a*)	12 (3)	H(16*b*)	10 (2)
H(16*c*)	10 (2)	*O(1)	6 (2)	*O(2)	9 (2)

Discussion. The structural work on *cis*-2,3,4a,6,7,8a-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, in the hope that the structural data would indicate the factors influencing the observed reaction pathways.

† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31851 (26 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.



(I)

A stereo diagram of the molecule, with the crystallographic numbering scheme, is shown in Fig. 1. The conformation is seen to be twisted about the C(5)–C(10) bond such that the bridgehead methyl groups are staggered. This conformation is common to the structures of all the related molecules so far determined in the course of the study. The degree of 'twist' is shown by the torsion angles C(6)–C(5)–C(10)–C(1) and C(13)–C(5)–C(10)–C(16) of −61·4 (5) and 60·0 (6)° respectively.

The two major photochemical reaction pathways for these 1,4-naphthoquinone systems involve either β-hydrogen abstraction from C(9) by O(1) or abstraction of one of the hydrogen atoms on C(6) by an enone carbon atom [C(2) or C(3)]. For (I) the distance O(1)···H(9*b*) of 2·47 (6) Å compared with an expected van der Waals O···H contact of about 2·60 Å suggests that the former reaction is feasible, especially as the *n* orbital of O(1) is favourably oriented. The distances C(2)···H(6*a*) and C(3)···H(6*a*) of 2·89 (6) and 2·80 (6) Å respectively also suggest the possibility of the second reaction. The solution photochemistry of (I) in benzene shows both pathways to be operating in competition (Scheffer, Trotter, Gayler & Bear, 1973) and the solid-state results only show a change in the product ratio (Dzakpasu, Phillips, Scheffer & Trotter, 1976).

The bond lengths and angles (see Tables 3 and 4) show normal values, except for the carbonyl C=O distances. The standard deviations quoted are probably underestimated due to the systematic error introduced by the disorder, and the anomalously short O(2)=C(4) distance is not likely to be significant. Most of the refined hydrogen-atom positions are reasonable but some are poor, for instance those in the C(12) methyl group. The close approach of H(11*a*) to O(1) [2·18 (6) Å] may well be a real effect arising from interaction of the H with the O lone pair.

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

O(1)—C(1)	1·232 (6)	O(2)–C(4)	1·185 (6)
C(1)—C(2)	1·492 (7)	C(1)–C(10)	1·537 (7)
C(2)—C(3)	1·340 (7)	C(3)–C(4)	1·486 (7)
C(4)—C(5)	1·517 (7)	C(5)–C(6)	1·528 (7)
C(5)—C(10)	1·547 (6)	C(6)–C(7)	1·520 (8)
C(7)—C(8)	1·323 (7)	C(8)–C(9)	1·507 (8)
C(9)—C(10)	1·541 (8)	C(2)–C(11)	1·494 (8)
C(3)—C(12)	1·494 (8)	C(5)–C(13)	1·547 (8)
C(7)—C(14)	1·533 (8)	C(8)–C(15)	1·525 (8)
C(10)–C(16)	1·532 (7)		

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

O(1)—C(1)—C(2)	121·3 (5)	O(1)–C(1)—C(10)	121·6 (5)
C(2)—C(1)—C(10)	117·1 (5)	C(1)–C(2)—C(3)	122·0 (4)
C(2)—C(3)—C(4)	120·0 (5)	O(2)–C(4)—C(3)	120·2 (5)
O(2)—C(4)—C(5)	121·9 (5)	C(3)–C(4)—C(5)	117·4 (5)
C(4)—C(5)—C(6)	110·5 (5)	C(4)–C(5)—C(10)	107·3 (5)
C(6)—C(5)—C(10)	109·2 (4)	C(5)–C(6)—C(7)	115·9 (6)
C(6)—C(7)—C(8)	121·2 (6)	C(7)–C(8)—C(9)	122·8 (5)
C(8)—C(9)—C(10)	114·7 (5)	C(1)–C(10)–C(5)	109·6 (4)
C(1)—C(10)–C(9)	108·3 (4)	C(5)–C(10)–C(9)	109·5 (5)
C(1)—C(2)—C(11)	118·7 (6)	C(3)–C(2)—C(11)	121·4 (6)
C(2)—C(3)—C(12)	124·8 (6)	C(4)–C(3)—C(12)	113·2 (6)
C(4)—C(5)—C(13)	108·3 (5)	C(6)–C(5)—C(13)	108·3 (5)
C(10)–C(5)—C(13)	112·8 (6)	C(6)–C(7)—C(14)	109·9 (6)
C(8)—C(7)—C(14)	127·4 (6)	C(7)–C(8)—C(15)	123·1 (6)
C(9)—C(8)—C(15)	115·7 (5)	C(1)–C(10)–C(16)	107·2 (5)
C(5)—C(10)–C(16)	113·0 (5)	C(9)–C(10)–C(16)	109·6 (5)

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.

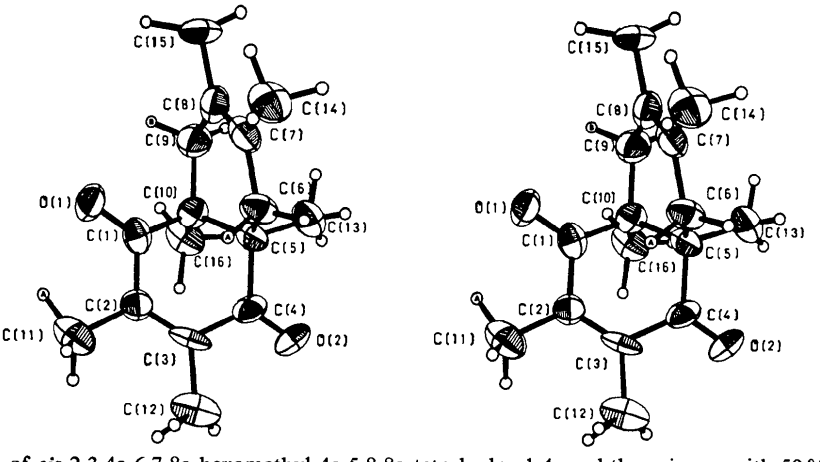


Fig. 1. Stereo diagram of *cis*-2,3,4a,6,7,8a-hexamethyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone with 50% probability vibration ellipsoids.

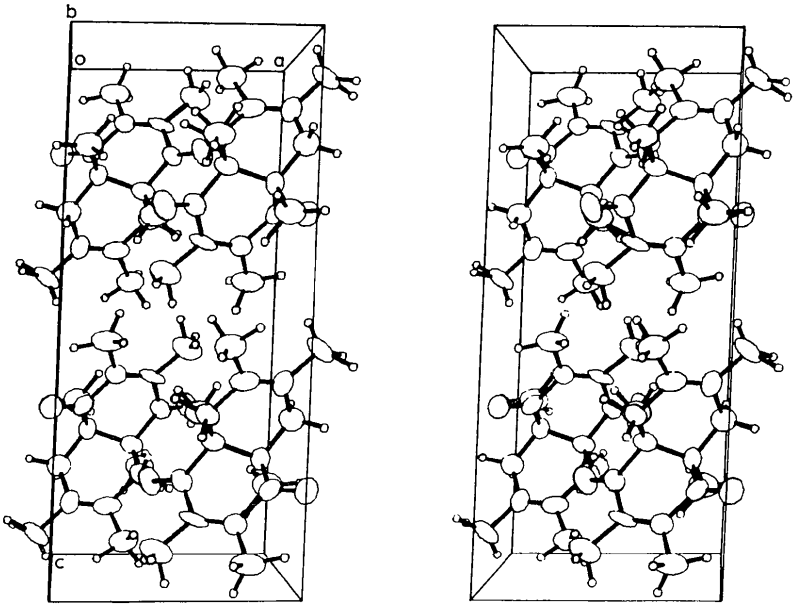


Fig. 2. Stereo diagram of the contents of the unit cell projected down the *b* axis.

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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, $C2/c$; $a=24{\cdot}930$ (7), $b=7{\cdot}795$ (3), $c=14{\cdot}472$ (5) Å, $\beta=101{\cdot}13$ (3)°; $d_m=1{\cdot}18$ (flotation), $d_x=1{\cdot}186$ g cm^{-3}, $Z=8$; μ(Cu $K\alpha$)$=6{\cdot}1$ cm^{-1}. The conformation of the molecule is twisted such that the bridgehead methyl groups are staggered with a torsion angle of 62·6°. 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 diffractometer 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 [$\sigma^2(I)=S+B+(0{\cdot}04S)^2$, where S = scan and B = background count]. Lorentz and polarization corrections were applied and the structure amplitudes derived. Crystal dimensions were approximately $0{\cdot}03\times0{\cdot}03\times0{\cdot}07$ 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