

6,7-Diphenyl-*cis*-4a,5,8,8a-tetrahydro-1,4-naphthoquinone

BY SIMON E. V. PHILLIPS AND JAMES TROTTER

Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada V6T 1W5

(Received 1 March 1976; accepted 29 April 1976)

Abstract. C₂₂H₁₈O₂, monoclinic, *C2/c*; $a=27.092$ (4), $b=6.527$ (2), $c=22.112$ (3) Å, $\beta=120.562$ (9)°; $d_m=1.23$ (floatation), $d_x=1.240$ g cm⁻³, $Z=8$; $\mu(\text{Cu } K\alpha)=6.3$ cm⁻¹. The conformation of the molecule is twisted such that the bridgehead hydrogen atoms are staggered with a torsion angle of 62°. Bond lengths and angles are close to normal values.

Introduction. Well formed yellow crystals were obtained by crystallization from methanol. Unit-cell and intensity data were measured on a Datex-automated G.E. XRD 6 diffractometer with Cu *K*α radiation and the θ - 2θ scan technique. Unit-cell parameters were refined by least squares from the observed 2θ values of 19 reflexions. Of the 3365 independent reflexions with $2\theta < 146^\circ$, 2648 had intensities greater than $3\sigma(I)$ above background [$\sigma^2(I) = S + B + (0.05S)^2$, where S = scan and B = background count]. Lorentz and polarization corrections were applied and the structure amplitudes derived. Crystal dimensions were $0.047 \times 0.043 \times 0.070$ cm and no absorption correction was applied.

The structure was solved in *C2/c* by direct methods with an automatic computer program (Long, 1965) to apply a multiresolution procedure to the 345 E values > 1.60 . All of the high consistency sets obtained gave E maps containing more than one image of the structure. The molecule was located in a map containing two images by placing it at the mean position. All non-hydrogen atoms were located in this way and refined for several cycles of full-matrix least squares 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 map then revealed the positions of all 18 hydrogen atoms and these were included in subsequent cycles of refinement. All non-hydrogen atoms were included with anisotropic temperature factors, the hydrogens being refined isotropically. 19 planes were zero weighted in the final cycles of refinement due to poor agreement revealed by the weighting statistics. The final R and R' $\{ = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} \}$ for the 2648 reflexions with $I > 3\sigma(I)$ are 0.053 and 0.078 respectively. For all 3365 data R is 0.069 and R' is 0.079. The error in an observation of unit weight, $[\sum w(|F_o| - |F_c|)^2 / (m - n)]^{1/2}$, is 1.94. Atomic scattering factors for O and C are those of Cromer & Mann (1968) and for H those of Stewart, Davidson & Simpson (1965). Final posi-

tional and thermal parameters are listed in Tables 1 and 2.*

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31855 (31 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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

	<i>x</i>	<i>y</i>	<i>z</i>
O(1)	1469 (1)	-3796 (2)	4277 (1)
O(2)	566 (1)	2192 (2)	5017 (1)
C(1)	1322 (1)	-2481 (3)	4545 (1)
C(2)	831 (1)	-2828 (4)	4647 (1)
C(3)	572 (1)	-1302 (3)	4772 (1)
C(4)	760 (1)	844 (3)	4815 (1)
C(5)	1186 (1)	1277 (3)	4584 (1)
C(6)	874 (1)	1540 (4)	3784 (1)
C(7)	1280 (1)	1653 (3)	3507 (1)
C(8)	1826 (1)	1026 (3)	3884 (1)
C(9)	2064 (1)	-21 (4)	4587 (1)
C(10)	1625 (1)	-466 (3)	4805 (1)
C(11)	1025 (1)	2454 (3)	2774 (1)
C(12)	783 (1)	4387 (4)	2591 (1)
C(13)	566 (1)	5118 (5)	1908 (1)
C(14)	570 (1)	3899 (5)	1408 (1)
C(15)	792 (1)	1953 (6)	1578 (1)
C(16)	1020 (1)	1229 (4)	2255 (1)
C(17)	2257 (1)	1360 (3)	3664 (1)
C(18)	2341 (1)	3291 (4)	3469 (1)
C(19)	2764 (1)	3618 (5)	3297 (1)
C(20)	3106 (1)	2030 (6)	3326 (1)
C(21)	3028 (1)	114 (6)	3517 (2)
C(22)	2611 (1)	-222 (4)	3686 (1)
H(2)	71 (1)	-420 (4)	461 (1)
H(3)	22 (1)	-150 (4)	482 (1)
H(5)	138 (1)	261 (4)	478 (1)
H(6a)	65 (1)	284 (4)	363 (1)
H(6b)	59 (1)	43 (4)	354 (1)
H(9a)	238 (1)	79 (4)	496 (1)
H(9b)	224 (1)	-130 (4)	457 (1)
H(10)	182 (1)	-58 (3)	530 (1)
H(12)	79 (1)	525 (4)	294 (2)
H(13)	39 (1)	646 (5)	180 (2)
H(14)	40 (1)	444 (5)	91 (2)
H(15)	79 (1)	102 (5)	122 (2)
H(16)	117 (1)	-21 (4)	239 (1)
H(18)	212 (1)	439 (4)	346 (1)
H(19)	280 (1)	505 (4)	316 (1)
H(20)	342 (1)	230 (4)	323 (1)
H(21)	327 (1)	-100 (5)	354 (2)
H(22)	256 (1)	-159 (4)	383 (1)

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 ($U_{ij} \times 10^3 \text{ \AA}^2$)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	77 (1)	46 (1)	87 (1)	-3 (1)	51 (1)	-14 (1)
O(2)	71 (1)	53 (1)	74 (1)	4 (1)	51 (1)	-6 (1)
C(1)	53 (1)	35 (1)	46 (1)	1 (1)	27 (1)	2 (1)
C(2)	66 (1)	41 (1)	69 (1)	-12 (1)	41 (1)	-2 (1)
C(3)	62 (1)	49 (1)	59 (1)	-9 (1)	41 (1)	0 (1)
C(4)	50 (1)	42 (1)	40 (1)	1 (1)	27 (1)	2 (1)
C(5)	50 (1)	32 (1)	46 (1)	-3 (1)	30 (1)	0 (1)
C(6)	47 (1)	48 (1)	47 (1)	9 (1)	29 (1)	11 (1)
C(7)	46 (1)	38 (1)	41 (1)	1 (1)	26 (1)	3 (1)
C(8)	46 (1)	34 (1)	44 (1)	1 (1)	27 (1)	2 (1)
C(9)	44 (1)	46 (1)	47 (1)	2 (1)	24 (1)	10 (1)
C(10)	44 (1)	36 (1)	34 (1)	-1 (1)	19 (1)	4 (1)
C(11)	41 (1)	49 (1)	40 (1)	1 (1)	22 (1)	5 (1)
C(12)	61 (1)	56 (1)	47 (1)	8 (1)	24 (1)	9 (1)
C(13)	63 (1)	70 (2)	58 (1)	5 (1)	19 (1)	22 (1)
C(14)	58 (1)	108 (2)	41 (1)	-9 (1)	21 (1)	15 (1)
C(15)	66 (1)	104 (2)	42 (1)	-1 (2)	28 (1)	-3 (1)
C(16)	54 (1)	69 (2)	47 (1)	2 (1)	29 (1)	-3 (1)
C(17)	41 (1)	50 (1)	40 (1)	-1 (1)	22 (1)	1 (1)
C(18)	53 (1)	53 (1)	52 (1)	-6 (1)	28 (1)	3 (1)
C(19)	68 (2)	79 (2)	60 (1)	-20 (1)	38 (1)	3 (1)
C(20)	59 (1)	110 (3)	72 (2)	-10 (2)	45 (1)	-2 (2)
C(21)	67 (2)	98 (2)	89 (2)	18 (2)	53 (2)	3 (2)
C(22)	63 (1)	61 (2)	74 (2)	10 (1)	45 (1)	7 (1)

(b) Isotropic thermal parameters ($U_{iso} \times 10^3 \text{ \AA}^2$)

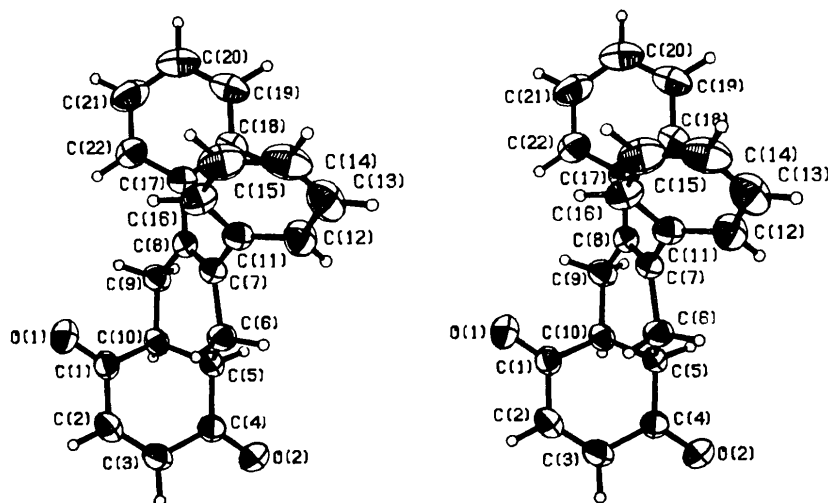
	U		U		U
H(2)	74 (8)	H(9b)	63 (7)	H(16)	64 (7)
H(3)	73 (8)	H(10)	38 (5)	H(18)	59 (7)
H(5)	51 (6)	H(12)	77 (8)	H(19)	68 (7)
H(6a)	51 (6)	H(13)	93 (10)	H(20)	84 (8)
H(6b)	65 (7)	H(14)	97 (9)	H(21)	97 (10)
H(9a)	63 (7)	H(15)	101 (10)	H(22)	74 (8)

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

		Cor- rected		Cor- rected	
O(1)—C(1)	1.220 (2)	1.221	O(2)—C(4)	1.219 (2)	1.220
C(1)—C(2)	1.477 (3)	1.479	C(1)—C(10)	1.501 (3)	1.506
C(2)—C(3)	1.325 (3)	1.328	C(3)—C(4)	1.477 (3)	1.482
C(4)—C(5)	1.509 (3)	1.511	C(5)—C(6)	1.534 (3)	1.539
C(5)—C(10)	1.535 (3)	1.539	C(6)—C(7)	1.511 (3)	1.513
C(7)—C(8)	1.339 (3)	1.343	C(8)—C(9)	1.511 (3)	1.516
C(9)—C(10)	1.522 (3)	1.524	C(7)—C(11)	1.496 (3)	1.500
C(8)—C(17)	1.492 (3)	1.496	C(11)—C(12)	1.383 (3)	1.390
C(11)—C(16)	1.393 (3)	1.402	C(12)—C(13)	1.397 (3)	1.401
C(13)—C(14)	1.368 (4)	1.377	C(14)—C(15)	1.374 (4)	1.380
C(15)—C(16)	1.380 (3)	1.385	C(17)—C(18)	1.388 (3)	1.396
C(17)—C(22)	1.393 (3)	1.402	C(18)—C(19)	1.394 (3)	1.398
C(19)—C(20)	1.369 (4)	1.378	C(20)—C(21)	1.371 (5)	1.378
C(21)—C(22)	1.376 (4)	1.380			

Thermal-motion analysis and correction of bond lengths for libration were carried out as for 2,3,4a β -,5 β ,8 β ,8a β -hexamethyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (Phillips & Trotter, 1976b) for the ten-atom core and the C=O bonds. The r.m.s. ΔU_{ij} for this rigid body is 0.0041 \AA^2 , compared to an r.m.s. $\sigma(U_{ij})$ of 0.0012 \AA^2 for the whole molecule, so the model is not perfect but the corrected bond lengths are likely to be a better approximation than those obtained from the original least-squares coordinates. Each phenyl ring was considered as a rigid body together with its adjoining carbon atom and the bond lengths were corrected within the system. The r.m.s. ΔU_{ij} is 0.0027 \AA^2 for the C(11)—C(16) ring and 0.0055 \AA^2 for the C(17)—C(22) ring. Corrected bond lengths are reported in Table 3. Bond angles were not significantly affected and corrected values are not reported.

Discussion. The structural work on 6,7-diphenyl-*cis*-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (I) was un-

Fig. 1. Stereo diagram of 6,7-diphenyl-*cis*-4a,5,8,8a-tetrahydro-1,4-naphthoquinone.

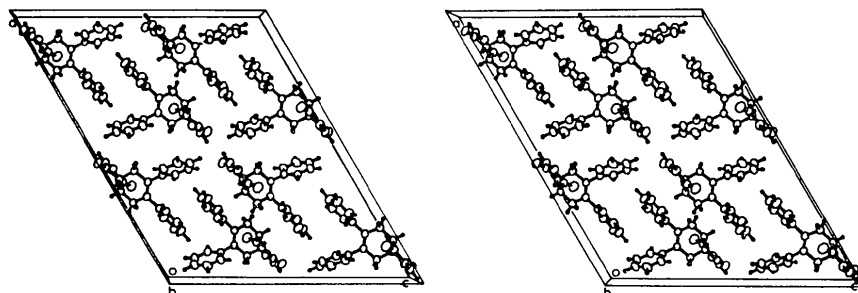
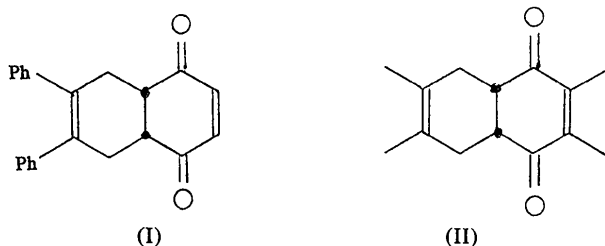


Fig. 2. Stereo diagram of the contents of the unit cell projected down the *b* axis.

dertaken as part of a study of the photochemistry of various substituted 1,4-naphthoquinone systems with *cis* bridgehead substituents (Phillips & Trotter, 1976*a*, *b*, *c*).



A stereo diagram of the molecule, with the crystallographic numbering scheme, is shown in Fig. 1. The conformation is staggered about the C(5)–C(10) bond as in 2,3,6,7-tetramethyl-*cis*-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (II) (Phillips & Trotter, 1976*c*). The torsion angles C(6)–C(5)–C(10)–C(1) and H(5)–C(5)–C(10)–H(10) are -67.9 (2) and 62 (2) $^\circ$ respectively, compared to corresponding values of -71.4 (4) and 56 (3) $^\circ$ in (II). Replacing the methyl groups at C(7) and C(8) with bulky phenyl rings has a significant effect on the torsion angles within the ring, some changing by as much as 10° . In particular the angle C(6)–C(7)–C(8)–C(9) is 0.2 (5) $^\circ$ in (II), showing that the four atoms form a good plane, but increases to 5.8 (2) $^\circ$ in (I). This is accompanied by a lengthening of the C(7)–C(8) bond. Torsion angles in the other ring show little change from the values found in (II).

Distances relevant to the expected photochemical reaction pathways, however, are not significantly different from those in (II). The carbonyl oxygen O(1) to β -hydrogen, H(9*b*), distance is 2.46 (3) Å, a difference of less than one standard deviation. H(6*b*) \cdots C(2) and H(6*b*) \cdots C(3) are 3.05 (3) and 2.97 (3) Å respectively, again close to the values in (II). Photolysis of (I) in solution gives a mixture of two products, an enone-alcohol and a diketone, both arising from the β -hydrogen abstraction pathway. Solid-state photolysis produces only the alcohol product (Dzakpasu, Phillips, Scheffer & Trotter, 1976).

Intermolecular distances mostly correspond to van der Waals contacts but there is one significant C–H \cdots

Table 4. Bond angles ($^\circ$) for non-hydrogen atoms with estimated standard deviations in parentheses

O(1)–C(1)–C(2)	120.7 (2)	O(1)–C(1)–C(10)	123.5 (2)
C(2)–C(1)–C(10)	115.8 (2)	C(1)–C(2)–C(3)	122.0 (2)
C(2)–C(3)–C(4)	121.7 (2)	C(3)–C(4)–C(5)	117.0 (2)
C(3)–C(4)–O(2)	120.7 (2)	C(5)–C(4)–O(2)	122.3 (2)
C(4)–C(5)–C(6)	110.0 (2)	C(4)–C(5)–C(10)	110.8 (2)
C(6)–C(5)–C(10)	109.5 (2)	C(5)–C(6)–C(7)	112.6 (2)
C(6)–C(7)–C(8)	122.3 (2)	C(7)–C(8)–C(9)	122.5 (2)
C(8)–C(9)–C(10)	114.8 (2)	C(1)–C(10)–C(5)	110.1 (2)
C(1)–C(10)–C(9)	114.1 (2)	C(5)–C(10)–C(9)	111.2 (2)
C(6)–C(7)–C(11)	115.2 (2)	C(8)–C(7)–C(11)	122.5 (2)
C(7)–C(8)–C(17)	123.5 (2)	C(9)–C(8)–C(17)	114.0 (2)
C(7)–C(11)–C(12)	121.7 (2)	C(7)–C(11)–C(16)	119.8 (2)
C(12)–C(11)–C(16)	118.5 (2)	C(11)–C(12)–C(13)	120.3 (3)
C(12)–C(13)–C(14)	120.2 (3)	C(13)–C(14)–C(15)	119.9 (2)
C(14)–C(15)–C(16)	120.4 (3)	C(11)–C(16)–C(15)	120.6 (3)
C(8)–C(17)–C(18)	120.9 (2)	C(8)–C(17)–C(22)	121.2 (2)
C(18)–C(17)–C(22)	117.8 (2)	C(17)–C(18)–C(19)	120.7 (2)
C(18)–C(19)–C(20)	120.1 (3)	C(19)–C(20)–C(21)	119.9 (2)
C(20)–C(21)–C(22)	120.4 (3)	C(17)–C(22)–C(21)	121.2 (3)

O interaction. The distance O(2) \cdots H(3) [$-x, -y, 1-z$] is 2.39 Å with favourable geometry, the normal van der Waals contact being about 2.6 Å. A stereo diagram of the crystal packing is shown in Fig. 2. Bond lengths and angles are given in Tables 3 and 4.

We thank Dr J. R. Scheffer for the crystals, the National Research Council of Canada for financial support and the University of British Columbia Computing Centre for assistance.

References

- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
- DZAKPASU, A. A., PHILLIPS, S. E. V., SCHEFFER, J. R. & TROTTER, J. (1976). *J. Amer. Chem. Soc.* Submitted for publication.
- LONG, R. E. (1965). Ph. D. Thesis, Univ. of California.
- PHILLIPS, S. E. V. & TROTTER, J. (1976*a*). *Acta Cryst.* **B32**, 3088–3091.
- PHILLIPS, S. E. V. & TROTTER, J. (1976*b*). *Acta Cryst.* **B32**, 3091–3094.
- PHILLIPS, S. E. V. & TROTTER, J. (1976*c*). *Acta Cryst.* **B32**, 3095–3097.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.