

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

A stereo diagram of the crystal packing is shown in Fig. 2.

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

- CHAN, S. I., BORGERS, T. R., RUSSELL, J. W., STRAUSS, H. L. & GWINN, W. D. (1966). *J. Chem. Phys.* **44**, 1103–1111.
- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
- HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.
- PHILLIPS, S. E. V. & TROTTER, J. (1976). *Acta Cryst.* **B32**, 3104–3106.
- PHILLIPS, S. E. V. & TROTTER, J. (1977). *Acta Cryst.* **B33**, 1599–1602.
- SCHEFFER, J. R. & DZAKPASU, A. A. (1975). Unpublished results.
- SCHEFFER, J. R., JENNINGS, B. M. & LOUWERENS, J. P. (1976). *J. Amer. Chem. Soc.* In the press.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1977). **B33**, 1605–1608

2,3-Dimethyl-1,4,4a,9a-tetrahydro-9,10-anthraquinone

BY SIMON E. V. PHILLIPS AND JAMES TROTTER

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

(Received 27 October 1976; accepted 3 January 1977)

Abstract. C₁₆H₁₆O₂, orthorhombic, *Pna*2₁, *a* = 15.643 (2), *b* = 5.160 (1), *c* = 15.568 (2) Å, *d*_m = 1.26, *d*_x = 1.270 g cm⁻³, *Z* = 4, μ(Cu Kα) = 6.6 cm⁻¹. The conformation of the molecule is twisted such that the bridgehead H atoms are staggered with a torsion angle of 57°. Bond lengths and angles are close to normal values.

Introduction. A small piece, dimensions ca 0.10 × 0.08 × 0.03 cm, was cut from a large, colourless, rod-shaped crystal and used for data collection. Unit-cell and intensity data were measured on a Datex-automated GE XRD 6 diffractometer with Cu Kα radiation and the θ–2θ scan technique. Unit-cell parameters were refined by least squares from the ob-

served 2θ values of 17 reflexions. Of the 1313 independent reflexions with $2\theta < 146^\circ$, 1233 had intensities greater than $3\sigma(I)$ above background [$\sigma^2(I) = S + B + (0.06S)^2$, where $S = \text{scan}$ and $B = \text{background count}$]. Lorentz and polarization corrections were applied and the structure amplitudes derived. No absorption correction was applied.

The structure was solved by direct methods with symbolic-addition and tangent-refinement techniques. The 203 E values greater than 1.35 were used for phase determination, origin-defining reflexions and starting symbols being chosen manually. The set of phases with the highest consistency gave an E map showing all non-hydrogen atoms except C(12) (see Fig. 1 for crystallographic numbering scheme). The coordinates of C(12) were estimated to give reasonable bond lengths. Several cycles of full-matrix least-squares refinement were carried out, where the function minimized was $\sum w(|F_o| - |F_c|)^2$. The initial weighting scheme was $w = 1.0$ but, in the later stages of refinement, planes with $|F_o| \geq 5.0$ were given weights $w = (5.0/|F_o|)^2$. The z coordinate of O(1) was fixed to define the origin along c . All H atoms were located on the difference map and included in the refinement with isotropic temperature factors. Non-hydrogen atoms were refined anisotropically.

In the final stages of refinement extinction effects were apparent in the data, and a correction was applied as described for 1,6-dicyano-2-hydroxy-8,9-dimethyl-tricyclo[4.4.0.0^{2,8}]dec-3,9-dien-5-one (Phillips & Trotter, 1977). The final refined value of the parameter E was $3.0(2) \times 10^{-7}$. The final R and $R' \{ = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} \}$ for the 1233 reflexions with $I > 3\sigma(I)$ are 0.040 and 0.052 respectively. For all 1313 data R is 0.042 and R' is 0.055. 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 parameters are listed in Table 1.*

Thermal-motion analysis and correction of bond lengths for libration was 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, 1976a). The tricyclic core, containing atoms C(1)–C(14), formed a good rigid body with a r.m.s. $\Delta U_{ij} = 0.0025 \text{ \AA}^2$. The r.m.s. $\sigma(U_{ij})$ from the least-squares refinement is 0.0013 \AA^2 . Peripheral bonds to O and methyl C atoms were corrected for independent motion. The effect of the correction is shown by the mean C–C distance in the aromatic ring which increased to 1.393(5) from the uncorrected value of 1.390(5) \AA . Corrected bond lengths are given in Table 2. Bond angles are not significantly affected and uncorrected values only are given in Table 3.

Discussion. The structure of 2,3-dimethyl-1,4,4a,9a-tetrahydro-9,10-anthraquinone (I) was determined as part of a study of the photochemistry of various substituted 1,4-naphthoquinone systems with *cis* bridgehead substituents. The structure of the related compound 2,3,6,7-tetramethyl-*cis*-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (II) has already been reported (Phillips & Trotter, 1976b).

A stereo diagram of the molecule, with the crystallographic numbering scheme, is shown in Fig. 1, the conformation being staggered about the C(5)–C(10) bond

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32403 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

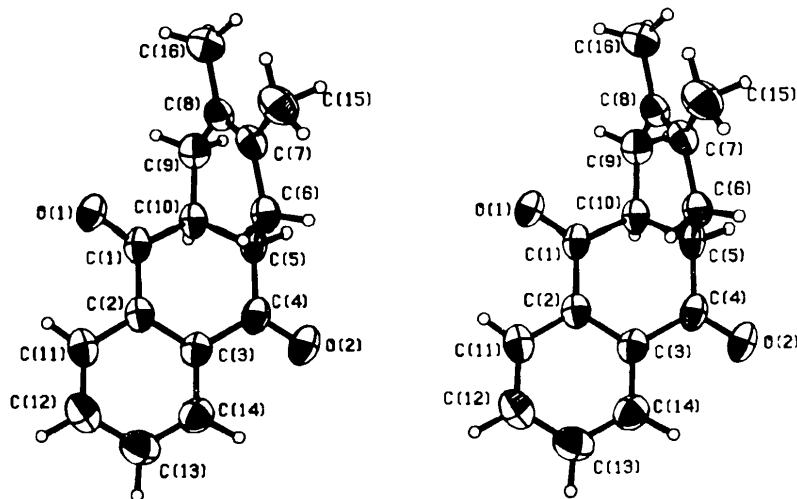


Fig. 1. Stereo diagram of 2,3-dimethyl-1,4,4a,9a-tetrahydro-9,10-anthraquinone showing the crystallographic numbering scheme.

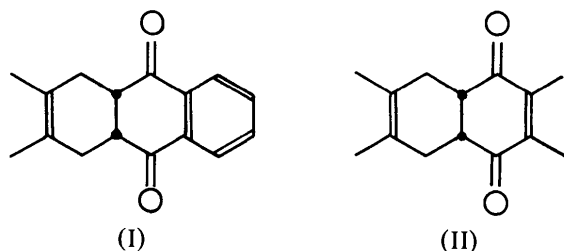


Table 1. *Final positional parameters (fractional, $\times 10^4$, $H \times 10^3$) with estimated standard deviations in parentheses*

	x	y	z
O(1)	7486 (1)	9085 (3)	3890
O(2)	5465 (2)	1669 (4)	5160 (2)
C(1)	7067 (2)	7192 (4)	4090 (2)
C(2)	6176 (2)	6869 (4)	3775 (2)
C(3)	5632 (2)	4987 (4)	4128 (2)
C(4)	5916 (2)	3385 (4)	4872 (2)
C(5)	6760 (2)	4061 (4)	5277 (2)
C(6)	6611 (2)	6167 (5)	5958 (2)
C(7)	7422 (2)	7404 (5)	6283 (2)
C(8)	8168 (2)	7142 (5)	5881 (2)
C(9)	8261 (2)	5624 (6)	5062 (2)
C(10)	7422 (2)	4987 (4)	4619 (2)
C(11)	5876 (2)	8409 (5)	3102 (2)
C(12)	5062 (2)	8109 (7)	2789 (3)
C(13)	4523 (2)	6267 (7)	3143 (2)
C(14)	4807 (2)	4708 (6)	3808 (2)
C(15)	7291 (3)	8994 (7)	7084 (2)
C(16)	8995 (2)	8313 (9)	6193 (3)
H(5)	697 (2)	246 (8)	554 (3)
H(6a)	631 (3)	551 (8)	642 (3)
H(6b)	618 (2)	744 (8)	575 (3)
H(9a)	866 (3)	644 (8)	468 (3)
H(9b)	857 (3)	390 (8)	523 (3)
H(10)	753 (2)	358 (6)	418 (3)
H(11)	625 (3)	959 (8)	290 (3)
H(12)	486 (3)	919 (7)	230 (3)
H(13)	395 (2)	614 (7)	291 (3)
H(14)	443 (3)	342 (7)	411 (3)
H(15a)	741 (4)	798 (11)	757 (5)
H(15b)	779 (3)	990 (9)	726 (4)
H(15c)	670 (5)	904 (13)	730 (6)
H(16a)	895 (4)	867 (14)	681 (5)
H(16b)	950 (3)	719 (10)	610 (3)
H(16c)	922 (4)	962 (15)	587 (6)

Table 2. *Bond lengths (\AA) for non-hydrogen atoms with estimated standard deviations in parentheses*

	Uncorrected	Corrected		Uncorrected	Corrected
O(1)—C(1)	1.217 (3)	1.218	O(2)—C(4)	1.218 (3)	1.218
C(1)—C(2)	1.487 (3)	1.491	C(1)—C(10)	1.510 (3)	1.516
C(2)—C(3)	1.407 (3)	1.413	C(2)—C(11)	1.397 (4)	1.401
C(3)—C(4)	1.489 (4)	1.493	C(3)—C(14)	1.390 (4)	1.391
C(4)—C(5)	1.503 (4)	1.507	C(5)—C(6)	1.536 (3)	1.542
C(5)—C(10)	1.533 (3)	1.539	C(6)—C(7)	1.507 (4)	1.511
C(7)—C(8)	1.330 (4)	1.336	C(7)—C(15)	1.508 (4)	1.507
C(8)—C(9)	1.503 (4)	1.508	C(8)—C(16)	1.509 (4)	1.507
C(9)—C(10)	1.518 (4)	1.521	C(11)—C(12)	1.372 (4)	1.375
C(12)—C(13)	1.384 (5)	1.389	C(13)—C(14)	1.385 (5)	1.387

as in (II). Torsion angles C(6)—C(5)—C(10)—C(1) and H(5)—C(5)—C(10)—H(10) are $-67.8(2)$ and $57(3)^\circ$ respectively, the corresponding values in (II) being $-71.4(4)$ and $56(3)^\circ$. Bond lengths and angles are not significantly different from those in (II), except for the increase in C(2)—C(3) resulting from the lower bond order. Intra-annular torsion angles are also very similar, with some small differences in the quinone ring.

The distance between the carbonyl oxygen O(1) and the β -hydrogen H(9a) is $2.60(5)$ \AA in (I), compared to $2.42(6)$ \AA in (II). Solution or solid-state photolysis of (I) induces β -H abstraction, resulting in the characteristic enone—alcohol product (Dzakpasu, Phillips, Scheffer & Trotter, 1976), while (II) is photoactive only in solution. Distances C(2) \cdots H(6b) and C(3) \cdots H(6b) are $3.09(4)$ and $2.96(4)$ \AA respectively, but photochemical abstraction of H(6b) by enone C is not observed in this case.

Mean-plane calculations show both carbonyl groups to be slightly, but significantly, non-planar. The aromatic ring is planar within experimental error, C(1) and C(4) deviating by 0.023 and -0.063 \AA respectively from the mean plane.

Intermolecular distances mainly correspond to van

Table 3. *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)	123.1 (2)
C(2)—C(1)—C(10)	116.1 (2)	C(1)—C(2)—C(3)	121.0 (2)
C(1)—C(2)—C(11)	120.0 (2)	C(3)—C(2)—C(11)	119.0 (2)
C(2)—C(3)—C(4)	120.4 (2)	C(2)—C(3)—C(14)	119.4 (2)
C(4)—C(3)—C(14)	120.0 (2)	O(2)—C(4)—C(3)	121.0 (3)
O(2)—C(4)—C(5)	121.6 (2)	C(3)—C(4)—C(5)	117.4 (2)
C(4)—C(5)—C(6)	108.7 (2)	C(4)—C(5)—C(10)	112.7 (2)
C(6)—C(5)—C(10)	110.0 (2)	C(5)—C(6)—C(7)	113.8 (2)
C(6)—C(7)—C(8)	122.5 (2)	C(6)—C(7)—C(15)	113.2 (2)
C(8)—C(7)—C(15)	124.3 (3)	C(7)—C(8)—C(9)	122.4 (2)
C(7)—C(8)—C(16)	124.0 (3)	C(9)—C(8)—C(16)	113.5 (3)
C(8)—C(9)—C(10)	114.5 (2)	C(1)—C(10)—C(5)	110.5 (2)
C(1)—C(10)—C(9)	113.7 (2)	C(5)—C(10)—C(9)	110.4 (2)
C(2)—C(11)—C(12)	120.9 (3)	C(11)—C(12)—C(13)	120.1 (3)
C(12)—C(13)—C(14)	120.1 (3)	C(13)—C(14)—C(3)	120.5 (3)

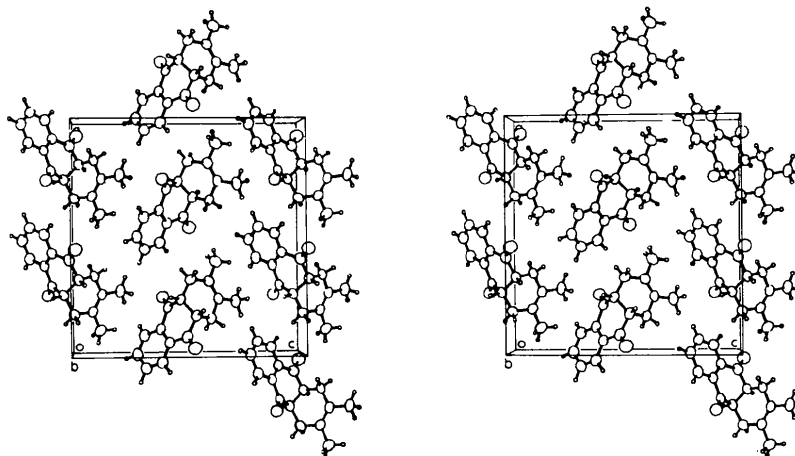


Fig. 2. Stereo diagram of the contents of the unit cell viewed down *b*.

der Waals contacts. One exception is the O(1)···H(10) [*x*, *y* + 1, *z*] distance of 2.34 Å, suggesting a C—H···O interaction. The C···O separation is 3.252 Å, and the angle subtended at H is 146°. A diagram of the crystal packing is shown in Fig. 2.

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.* **98**, 6049–6051.
 PHILLIPS, S. E. V. & TROTTER, J. (1976a). *Acta Cryst.* **B32**, 3091–3094.
 PHILLIPS, S. E. V. & TROTTER, J. (1976b). *Acta Cryst.* **B32**, 3095–3097.
 PHILLIPS, S. E. V. & TROTTER, J. (1977). *Acta Cryst.* **B33**, 1599–1602.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1977). **B33**, 1608–1610

Le Dichlorure de Calcium Dihydraté*

PAR A. LECLAIRE ET M. M. BOREL

Laboratoire de Cristallographie et Chimie du Solide associé au CNRS n° 251, Laboratoires de Cristallographie—Minéralogie et de Chimie Minérale B, UER des Sciences, Université de Caen, 14032 Caen Cédex, France

(Reçu le 17 décembre 1976, accepté le 5 janvier 1977)

Abstract. CaCl₂·2H₂O, orthorhombic, *Pbcn*; *a* = 5.893 (3), *b* = 7.469 (2), *c* = 12.070 (2) Å, *V* = 531.3 Å³, *D_m* = 1.86 g cm⁻³, *Z* = 4, *μ*(Mo *Kα*)/*ρ* = 10.8 cm² g⁻¹. The compound crystallized at 62°C from a supersaturated aqueous solution of CaCl₂. The struc-

ture consists of layers, held together by hydrogen bonds, parallel to the *ab* plane. The Ca atom is linked to four Cl and two O atoms.

Introduction. Les cristaux de CaCl₂·2H₂O ont été obtenus en laissant se concentrer dans un thermostat à 62°C une solution aqueuse de chlorure de calcium.

* Etude des Halogénures de Calcium. I.