

Discussion. Bond lengths and angles (Fig. 1) are consistent with those observed in other related compounds (Hite & Craven, 1973; Hite & Soares, 1973; Ruble, Blackmond & Hite, 1976; Ruble, Hite & Soares, 1976*a,b*). The benzene ring is equatorial and *cis* to the tertiary hydroxyl group. The ($\alpha R, 1R, 2R-\alpha S, 1S, 2S$) stereochemistry of this racemate confirms the *cis-threo* assignment of structure made earlier on the basis of PMR and chemical data (Thomas, Davidson, Griffith & Scott, 1976). The tertiary hydroxyl groups are intramolecularly hydrogen bonded to the carbonyl O atoms (Figs. 1 and 2). Enantiomeric pairs of molecules are dimerized through head-to-tail hydrogen bonding to give classic, planar eight-membered rings which are nearly parallel to the planes of the aromatic rings. These conformational features are defined by the torsion angles shown in Fig. 1. The hydrophilic groups are sandwiched between the hydrophobic aromatic rings of the dimers. There are no other hydrogen bonds. Thus, the dimeric units are held together in the lattice by ring stacking approximately along the *z* axis, by

other interactions and possibly by long-range dipolar interactions. All intermolecular C...C distances are greater than 3.82 Å.

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3,4,6,8 β ,9,10-Hexamethyltetracyclo[4.3.1.0^{3,10}.0^{4,9}]decane-2,5-dione

BY TREVOR J. GREENHOUGH AND JAMES TROTTER

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

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Abstract. C₁₆H₂₂O₂, triclinic, $P\bar{1}$, $a = 7.7672$ (10), $b = 8.7689$ (6), $c = 10.3545$ (6) Å, $\alpha = 85.589$ (5), $\beta = 76.909$ (7), $\gamma = 89.228$ (7)°, $Z = 2$, $D_x = 1.19$ Mg m⁻³, $\mu(\text{Cu } K\alpha) = 0.568$ mm⁻¹; $R = 0.042$ for 2487 reflexions. This novel tetracyclic solution photo-product is completely different from that obtained in the solid state and bears little resemblance to the 1,4-naphthoquinone derivative from which it is formed. The crystal structure consists of discrete molecular units with bond distances and angles which suggest a highly strained system.

Introduction. Recrystallization from CCl₄ afforded large colourless chunks from which a fragment of dimensions *ca* 0.2 × 0.3 × 0.4 mm was cut. A series of precession photographs provided an initial unit cell and the Laue symmetry $\bar{1}$. Accurate unit-cell parameters were determined by least-squares analysis of the setting angles of 25 reflections ($70 < \theta < 75^\circ$, Ni-filtered Cu $K\alpha$ radiation) automatically located and centred on an Enraf–Nonius CAD-4 diffractometer. The intensities

were collected with an $\omega-2\theta$ scan, $\Delta\omega = (1.0 + 0.15 \tan \theta)^\circ$, an aperture 4 mm high and $(1.5 + 0.5 \tan \theta)$ mm wide, a pre-scan acceptance limit of 6σ at $5.03^\circ \text{ min}^{-1}$ and a maximum recording time of 180 s. Of 2822 recorded intensities out to $\theta = 75^\circ$, 2487 (88%) had $I/\sigma(I) \geq 3$ with $\sigma^2(I) = S + B + (0.04S)^2$ (S being the scan and B the background count). During the data collection three standard reflections were checked periodically and their intensities showed a steady decrease to 96% of their initial value; this was corrected for during data processing where Lorentz and polarization corrections were applied. Absorption correction using a Gaussian integration method gave transmission factors for I varying between 0.769 (930) and 0.914 (011).

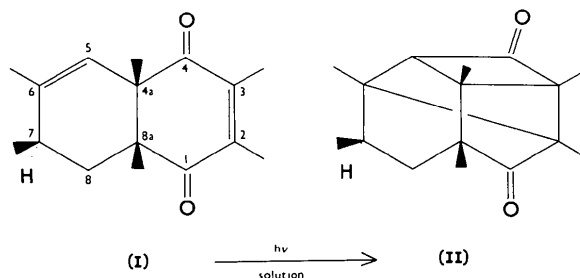
All non-hydrogen atoms were located by direct methods; the $|E|$ statistics clearly indicated the centrosymmetric space group. With all atoms refined as C in isotropic full-matrix least squares, the O atoms were clearly identified by their abnormally low thermal parameters.

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>
C(1)	4260 (2)	2688 (1)	1040 (1)
C(2)	2384 (2)	2094 (2)	1460 (1)
C(3)	1598 (2)	3283 (2)	2482 (1)
C(4)	427 (2)	2333 (2)	3619 (1)
C(4a)	3063 (2)	2975 (1)	3328 (1)
C(5)	2038 (2)	1407 (2)	3772 (1)
C(6)	2491 (2)	605 (1)	2473 (1)
C(7)	4399 (2)	-15 (2)	2252 (1)
C(8)	5598 (2)	1202 (2)	2585 (2)
C(8a)	4859 (2)	2808 (2)	2326 (1)
C(9)	1491 (3)	1915 (2)	325 (2)
C(10)	1129 (2)	4857 (2)	1988 (2)
C(11)	3008 (3)	3997 (2)	4452 (2)
C(12)	1145 (3)	-627 (2)	2420 (2)
C(13)	4569 (3)	-1540 (2)	3027 (2)
C(14)	6200 (2)	4085 (2)	2233 (2)
O(1)	5109 (2)	2973 (1)	-79 (1)
O(4)	-1062 (2)	2445 (2)	4246 (1)
H(5)	207 (2)	79 (2)	466 (2)
H(7)	477 (2)	-18 (2)	130 (2)
H(81)	566 (2)	107 (2)	356 (2)
H(82)	684 (3)	111 (2)	204 (2)
H(91)	202 (3)	105 (3)	-20 (2)
H(92)	168 (3)	285 (3)	-30 (2)
H(93)	22 (3)	168 (2)	60 (2)
H(101)	218 (3)	540 (3)	143 (2)
H(102)	67 (3)	548 (3)	273 (2)
H(103)	12 (3)	480 (3)	158 (2)
H(111)	386 (3)	365 (3)	496 (2)
H(112)	334 (3)	504 (2)	409 (2)
H(113)	176 (4)	398 (3)	511 (3)
H(121)	107 (3)	-141 (3)	320 (2)
H(122)	-9 (3)	-18 (3)	243 (2)
H(123)	147 (3)	-112 (2)	157 (2)
H(131)	391 (3)	-243 (2)	273 (2)
H(132)	409 (3)	-148 (2)	399 (2)
H(133)	586 (3)	-179 (3)	292 (2)
H(141)	567 (3)	514 (2)	204 (2)
H(142)	667 (3)	402 (2)	300 (2)
H(143)	722 (3)	392 (3)	145 (2)

Following anisotropic refinement of C and O, the H atoms were located from a difference map and were assigned isotropic thermal parameters. Scattering factors for H were taken from Stewart, Davidson & Simpson (1965) and all others were from Cromer & Mann (1968). The final refinements included all atomic parameters and an isotropic extinction parameter g (Becker & Coppens, 1974, 1975) and gave $R = 0.042$ ($R = \sum |\Delta F| / \sum |F_o|$) for the 2487 observed reflections. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F)$, giving $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.047$ and σ_1 (GOF) = 2.3. The mean and maximum shift/error on the final cycle of least squares were 0.002 and 0.021, respectively, and the final value of $g = 2.8(4) \times 10^3$. A difference synthesis after the final cycle showed random fluctuations of up to $\pm 0.2 e \text{ \AA}^{-3}$. Final atomic coordinates are presented in Table 1.*

Discussion. The photochemical study of 2,3,4a β ,6,7 β ,8a β -hexamethyl-4a,7,8,8a-tetrahydro-1,4-naphthoquinone (I) has provided the first example of complete unimolecular solid-state/solution reactivity differences (Appel, Greenhough, Scheffer & Trotter, 1979).



The crystal structure of the starting diketone (I) (Greenhough & Trotter, 1980) allowed a reaction pathway for the formation of the solid-state product (Scheffer, Bhandari, Gayler & Wostradowski, 1975) to be proposed. Elucidation of the structure of the solution photoproduct 3,4,6,8 β ,9,10-hexamethyltetracyclo[4.3.1.0^{3,10}.0^{4,9}]decane-2,5-dione (II) was undertaken in order that a photochemical reaction pathway in solution and reasons for the solid-state/solution reactivity differences might be proposed.

The molecular structure of the novel tetracyclic solution photoproduct (II) is shown in Fig. 1, where the atomic numbering of the starting diketone (I) (Greenhough & Trotter, 1980) is retained. On the basis of the structural results for (I) and (II) the solution photochemical conversion has been proposed as a

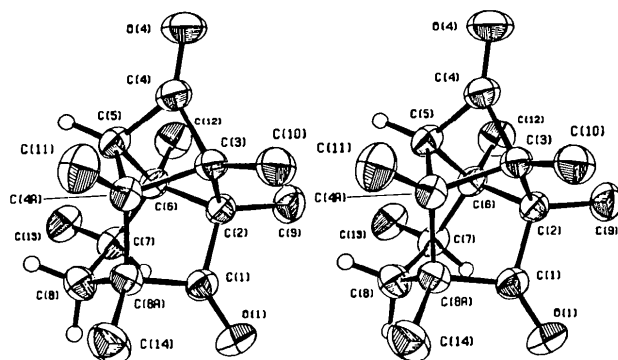


Fig. 1. Stereodiamgram of 3,4,6,8 β ,9,10-hexamethyltetracyclo[4.3.1.0^{3,10}.0^{4,9}]decane-2,5-dione showing the crystallographic numbering scheme. Thermal ellipsoids are at the 50% probability level.

* Lists of thermal parameters, intermolecular distances (Table 4), a packing diagram (Fig. 2), and a list of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34671 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

molecular rearrangement, initiated by C(4) to C(5) bridging, which requires relatively large atomic and molecular motion (Appel, Greenhough, Scheffer & Trotter, 1979). It appears that crystal-lattice or topochemical control prevents the formation of (II) in the solid state, where the basic molecular shape of (I) is retained throughout the proposed photochemical transformation (Appel, Greenhough, Scheffer & Trotter, 1979).

Bond distances and angles are given in Tables 2 and 3 according to the atomic numbering in Fig. 1. All three six-membered rings are in distorted twist-boat conformations with bond distances and angles which suggest a highly strained system. The C(2)–C(6) [0^{4,9}] bridge is unusually long at 1.624 (2) Å and is accompanied by deviations of up to 12° from the normal tetrahedral angle at C(2) [99.1 (1)–118.1 (1)°] and C(6) [97.7 (1)–112.6 (1)°]. This long C–C distance could be caused in part by the Me(9)–Me(12) steric interaction, with a torsion angle of 19° about C(2)–C(6); bond angles at C(2) are consistent with this possibility. The four-membered ring is puckered with the C(sp²)–C(sp³) bonds normal at 1.514 (2) and 1.515 (2) Å, and long C(sp³)–C(sp³) distances of 1.582 (2) Å, and 1.594 (2) Å for the C(3)–C(4a) [0^{3,10}] bridge; O(4) and C(4a) deviate by 0.15 and 0.87 Å, respectively, from the C(3), C(4), C(5) plane, with the torsional strain being relieved by angle strains to give endocyclic angles between 83.4 (4)° at C(4a) and 88.4 (1)° at the sp²-hybridized C(4). The O(4) and Me(10) substituents are eclipsed, the distortions at C(3) being further evidenced by the angles involving Me(10), which range from 119.5 (1) to 123.8 (1)°, and the C(2)–C(3)–C(4a) angle of 93.9 (1)°. The five-membered rings

Table 2. Bond distances (Å) ($\sigma = 0.002$ Å for C–C, C–O, 0.02–0.03 Å for C–H)

C(1)–C(2)	1.511	C(5)–C(4)	1.515
C(2)–C(3)	1.563	C(4)–C(3)	1.514
C(3)–C(4a)	1.594	C(2)–C(6)	1.624
C(4a)–C(8a)	1.551	C(2)–C(9)	1.512
C(8a)–C(1)	1.519	C(3)–C(10)	1.504
C(8a)–C(8)	1.541	C(4a)–C(11)	1.516
C(8)–C(7)	1.535	C(6)–C(12)	1.527
C(7)–C(6)	1.546	C(7)–C(13)	1.525
C(6)–C(5)	1.533	C(8a)–C(14)	1.522
C(5)–C(4a)	1.582	C(1)–O(1)	1.206
		C(4)–O(4)	1.198
C(5)–H(5)	1.03	C(11)–H(112)	0.98
C(7)–H(7)	0.99	C(11)–H(113)	1.05
C(8)–H(81)	1.02	C(12)–H(121)	1.01
C(8)–H(82)	1.01	C(12)–H(122)	1.03
C(9)–H(91)	0.99	C(12)–H(123)	0.99
C(9)–H(92)	0.99	C(13)–H(131)	1.04
C(9)–H(93)	0.98	C(13)–H(132)	0.98
C(10)–H(101)	0.99	C(13)–H(133)	1.01
C(10)–H(102)	0.98	C(14)–H(141)	1.03
C(10)–H(103)	0.97	C(14)–H(142)	0.95
C(11)–H(111)	0.96	C(14)–H(143)	1.02

Table 3. Inter-bond angles (°) ($\sigma = 0.1^\circ$)

C(2)–C(1)–C(8a)	105.2	C(3)–C(4a)–C(5)	83.4
C(2)–C(1)–O(1)	127.3	C(3)–C(4a)–C(11)	116.3
O(1)–C(1)–C(8a)	127.5	C(3)–C(4a)–C(8a)	107.2
C(1)–C(2)–C(3)	99.1	C(5)–C(4a)–C(11)	114.1
C(1)–C(2)–C(6)	104.6	C(5)–C(4a)–C(8a)	113.4
C(1)–C(2)–C(9)	114.6	C(8a)–C(4a)–C(11)	117.6
C(3)–C(2)–C(6)	99.9	C(2)–C(6)–C(5)	97.7
C(3)–C(2)–C(9)	117.8	C(2)–C(6)–C(7)	110.8
C(6)–C(2)–C(9)	118.1	C(2)–C(6)–C(12)	112.6
C(2)–C(3)–C(4a)	93.9	C(5)–C(6)–C(7)	109.6
C(2)–C(3)–C(4)	104.0	C(5)–C(6)–C(12)	112.6
C(2)–C(3)–C(10)	119.5	C(7)–C(6)–C(12)	112.6
C(4)–C(3)–C(4a)	84.0	C(6)–C(7)–C(8)	108.9
C(4)–C(3)–C(10)	123.8	C(6)–C(7)–C(13)	114.2
C(4a)–C(3)–C(10)	123.2	C(8)–C(7)–C(13)	110.8
C(3)–C(4)–C(5)	88.4	C(4a)–C(8a)–C(1)	101.2
C(3)–C(4)–O(4)	134.5	C(4a)–C(8a)–C(8)	108.6
C(5)–C(4)–O(4)	136.1	C(4a)–C(8a)–C(14)	116.3
C(4)–C(5)–C(6)	102.1	C(1)–C(8a)–C(8)	103.0
C(4)–C(5)–C(4a)	84.4	C(1)–C(8a)–C(14)	112.9
C(4a)–C(5)–C(6)	101.1	C(8)–C(8a)–C(14)	113.4
		C(7)–C(8)–C(8a)	109.8

C(2), C(3), C(4), C(5), C(6) and C(2), C(3), C(4a), C(5), C(6) are slightly distorted envelopes with C(4) and C(4a) deviating by –0.95 and 1.13 Å, respectively, from the mean plane through C(2), C(3), C(5), C(6). The other five-membered ring is a more distorted envelope, with C(2) and C(4a) deviating by 0.78 and 0.20 Å, respectively, from the C(1), C(3), C(8a) plane. The C(1)=O(1) carbonyl group is slightly non-planar, O(1) deviating by 0.02 Å (20 σ) from the C(1), C(2), C(8a) plane. O(1) and C(9) are eclipsed with a C(2)–C(1) torsion angle of –2.8 (2)°. Bond lengths and angles other than those involving atoms in the bridges or the four-membered ring are generally near expected values. The substituents at C(8a), C(8) and C(7) are staggered, with the methyl groups pseudo-equatorial to the C(2), C(1), C(8a), C(8), C(7), C(6) ring.

Intermolecular contacts generally correspond to van der Waals distances. A selection of intermolecular non-bonded distances is given in Table 4* and the crystal packing is illustrated in Fig. 2.*

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* See deposition footnote.

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Hexachloroquinoxaline

By A. J. W. A. VERMEULEN AND C. HUISZON*

Chemical Physics Laboratory, Twente University of Technology, PO Box 217, Enschede, The Netherlands

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Abstract. C₈Cl₆N₂, monoclinic, *P*2₁/*c*, *a* = 13.168 (1), *b* = 3.9178 (4), *c* = 21.622 (3) Å, β = 101.22 (2)° at 293 K; *D*_x = 2.045 (1) Mg m⁻³ with *Z* = 4; Mo *K* α radiation (λ = 0.7107 Å); *R*_w = 0.068. The molecule is planar despite close intramolecular contacts between Cl atoms.

Introduction. A crystal of the title compound was obtained from Dr D. M. W. van den Ham of our laboratory. It was prepared by the method of Allison, Chambers, MacBride & Musgrave (1971). The crystal was needle-shaped with *b* as the long axis. The diameter was about 0.2 mm and the length 0.7 mm. Data were collected at room temperature, 293 K, with a computer-controlled diffractometer (Philips PW 1100), and graphite-monochromated Mo *K* α radiation. The built-in program for the determination of lattice constants (Hornstra & Vossers, 1973) was used.

Each set of the four equivalent reflexions *hkl*, *h \bar{k} l*, *h \bar{k} l* and *h \bar{k} l* was recorded in the θ range 2.5 to 30°, with the ω -2 θ scan mode, scan width 1.2°, scan speed 0.1° s⁻¹, horizontal detector aperture 2.0° and vertical detector aperture 1.5°. Background counting was for one half of the total scan time at each side of the reflexion.

As μ = 1.55 mm⁻¹, absorption corrections were applied. The resulting correction factors for the intensities ranged from 0.75 to 0.82.

The intensities of the non-equivalent reflexions were obtained as weighted means of the intensities of equivalent reflexions.

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971). From the *E* map all atom

positions were found. The refinement was carried out with a modified version of *ORFLS* (Busing, Martin & Levy, 1962). The function minimized was $\sum w(|F_o| - k|F_c|)^2$. The weight, *w*, for each reflexion was taken to be $w = \sigma^{-2}$ with $\sigma = s + 0.01|F_o|$, where *s* denotes the e.s.d. in $|F_o|$ due to counting statistics. To calculate *s* from the statistical error in the measured intensities, a normal distribution in $|F_o|$ was assumed (Rees, 1976). Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The parameters varied in the last cycle were: positional parameters and anisotropic thermal parameters of all atoms, an isotropic extinction factor (Larson, 1969)

Table 1. *Fractional coordinates for hexachloroquinoxaline*

E.s.d.'s are shown in parentheses and refer to the last digit.

	<i>x</i>	<i>y</i>	<i>z</i>
N(1)	0.6752 (2)	0.6571 (9)	0.0008 (1)
C(2)	0.7348 (3)	0.566 (1)	-0.0366 (2)
C(3)	0.8299 (3)	0.391 (1)	-0.0151 (2)
N(4)	0.8606 (2)	0.3086 (9)	0.0437 (1)
C(5)	0.8296 (3)	0.322 (1)	0.1494 (2)
C(6)	0.7664 (3)	0.404 (1)	0.1904 (2)
C(7)	0.6712 (3)	0.574 (1)	0.1689 (2)
C(8)	0.6409 (2)	0.657 (1)	0.1061 (2)
C(9)	0.7051 (3)	0.572 (1)	0.0631 (2)
C(10)	0.7987 (3)	0.402 (1)	0.0848 (2)
Cl(11)	0.69707 (9)	0.6649 (3)	-0.11521 (5)
Cl(12)	0.90803 (8)	0.2680 (4)	-0.06640 (5)
Cl(13)	0.94702 (7)	0.1299 (3)	0.17513 (5)
Cl(14)	0.80247 (8)	0.3113 (3)	0.26904 (5)
Cl(15)	0.59167 (8)	0.6686 (3)	0.22067 (5)
Cl(16)	0.52662 (7)	0.8682 (3)	0.07883 (5)

* To whom correspondence should be addressed.