requirements for intramolecular 2 + 2 cycloaddition than do the observed solid-state conformers A and B. The solid-state/solution reactivity differences in both the 4α-ol and the 4β-ol thus appear to be due to crystal-lattice control of the photorearrangement via control of molecular conformation, as distinct from control in the sense of a least-motion process as found for 2,3,4aβ,6,7β,8aβ-hexamethyl-4a,7,8,8a-tetrahydro-1,4-naphthoquinone (Appel, Greenhough, Scheffer & Trotter, 1979; Greenhough & Trotter, 1979, 1980), where the completely different unimolecular photorearrangements in solution and the solid state are assumed to proceed from the same molecular conformation.

The bond lengths and angles in both molecules (Table 3) have normal values. The six-membered rings all have half-chair conformations: in the 4α-ol molecule, C(4a) and C(8a) deviate by −0·48 and 0·25 Å from the mean plane of C(1) to C(4), and by 0·42 and −0·33 Å from the mean plane of C(5) to C(8); the corresponding displacements in the 4β-ol are −0·53 and 0·20, and 0·33 and −0·42 Å. The carbonyl groups are only slightly non-planar, with C(1) out of plane by 0·03 Å (23σ) in the 4α-ol, and by 0·02 Å (9σ) in the 4β-ol. The twist conformation produces two close intramolecular H···H contacts in the 4β-ol, H(52)···H(O4) = 2·18 (4) and H(82)···H(4) = 2·27 (3) Å; such short contacts are not present in the 4α-ol.

Molecules in both crystals are linked into chains along a by O(4)—H(O4)···O(1) intermolecular hydrogen bonds, O(4)···O(1) = 2·802 (1) and 2·846 (2) Å in the 4α-ol and 4β-ol, respectively, H(O4)···O(1) = 1·98 (2) and 2·06 (3) Å, O(4)—H(O4)···O(1) = 171 and 167°. Packing diagrams have been deposited.

References

APPEL, W. K., GREENHOUGH, T. J., SCHEFFER, J. R. & TROTTER, J. (1979). *J. Am. Chem. Soc.* **101**, 213–215.
APPEL, W. K., GREENHOUGH, T. J., SCHEFFER, J. R., TROTTER, J. & WALSH, L. (1980). *J. Am. Chem. Soc.* **102**, 1158–1161.
BECKER, P. J. & COPPENS, P. (1974). *Acta Cryst.* A**30**, 129–147.
BECKER, P. J. & COPPENS, P. (1975). *Acta Cryst.* A**31**, 417–425.
CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.
GREENHOUGH, T. J. & TROTTER, J. (1979). *Acta Cryst.* B**35**, 3084–3087.
GREENHOUGH, T. J. & TROTTER, J. (1980). *Acta Cryst.* B**36**, 368–373.
LADD, M. F. C. (1978). Private communication.
MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J. P. & WOOLFSON, M. M. (1978). *MULTAN 78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.
PHILLIPS, S. E. V. & TROTTER, J. (1976). *Acta Cryst.* B**32**, 3088–3091.
PHILLIPS, S. E. V. & TROTTER, J. (1977). *Acta Cryst.* B**33**, 996–1003.
SCHEFFER, J. R. & DZAKPASU, A. A. (1978). *J. Am. Chem. Soc.* **100**, 2163–2173.
SCHMIDT, G. M. J. (1971). *Pure Appl. Chem.* **27**, 647–678.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Crystal Structures of 2,3,4aβ,8aβ-Tetramethyl-4a,5,8,8a-tetrahydro-1-naphthoquin-4β-ol* and Its Solid-State Photoproduct

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Abstract

Crystals of the naphthoquinol are monoclinic, $P2_1/n$, $a = 7\cdot319$ (2), $b = 11\cdot140$ (1), $c = 15\cdot510$ (3) Å,

$\beta = 96\cdot41$ (3)°, $Z = 4$, $R = 0\cdot048$ for 931 reflexions. The photoproduct is triclinic, $P\bar{1}$, $a = 6\cdot981$ (1), $b = 7\cdot619$ (2), $c = 11\cdot776$ (2) Å, $\alpha = 77\cdot70$ (1), $\beta = 85\cdot58$ (1), $\gamma = 79\cdot54$ (2)°, $Z = 2$, $R = 0\cdot070$ for 1126 reflexions. The naphthoquinol molecule has a conformation which has the hydroxyl group pseudo-

* IUPAC name: 4β-hydroxy-2,3,4aβ,8aβ-tetramethyl-4a,5,8,8a-tetrahydro-1(4H)-naphthalenone.

equatorial, with a short C···H intramolecular non-bonded contact which accounts for the solid-state photoreactivity and for the nature of the photoproduct. The molecules are linked in the crystals by O—H···O hydrogen bonds to form chains in the naphthoquinol and centrosymmetric dimers in the photoproduct.

Introduction

As part of a study of the photochemistry of tetra-hydronaphthoquinols (Appel, Greenhough, Scheffer, Trotter & Walsh, 1980; Greenhough & Trotter, 1980), the crystal structure of 2,3,4aβ,8aβ-tetramethyl-4a,5,8,8a-tetrahydro-1-naphthoquin-4β-ol (I) has been investigated. In addition, since the structure of the solid-state photoproduct could not be readily deduced by chemical methods, it has been determined by crystal structure analysis, and shown to be (II).
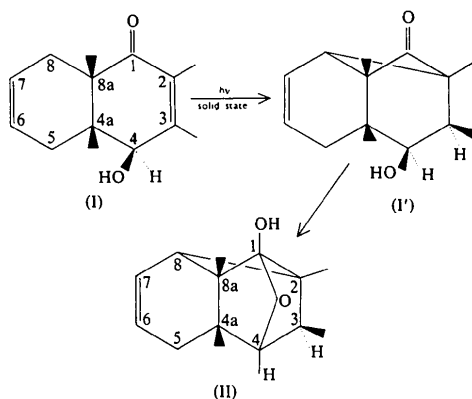
Experimental

Crystals were grown from n-hexane and CH_2Cl_2 solutions for the naphthoquinol and the photoproduct, respectively. Unit-cell, space-group, and intensity data were measured on the CAD-4 diffractometer as for the hexamethyltetrahydronaphthoquinols (Greenhough & Trotter, 1980); the data and the experimental conditions are summarized in Table 1.

The structure analyses proceeded as for the hexamethyl compounds, with use of K-curve scaling, MULTAN, difference syntheses, and full-matrix least-squares refinements (Table 1). The refinement of the naphthoquinol structure proceeded smoothly; mean and maximum shift/error on the final cycle were 0·14 and 2·3 (the larger shifts for H parameters), suitability of the weighting scheme $[w = 1/\sigma^2(F)]$ was confirmed, and a final difference Fourier synthesis had random fluctuations of up to $\pm$0·25 e Å^{-3}. Some difficulties were encountered with poor definition of methyl H atoms and of H(O4), but most H atoms behaved well in the refinement; in particular, H(82), whose position

Table 1. *Experimental data*

	Naphthoquinol*	Photoproduct†
Formula	$C_{14}H_{20}O_2$	$C_{14}H_{20}O_2$
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$ (C_{2h}^5)	$P\bar{1}$ (C_i^1)
a (Å)	7·319 (2)	6·981 (1)
b (Å)	11·140 (1)	7·619 (2)
c (Å)	15·510 (3)	11·776 (2)
α (°)	–	77·70 (1)
β (°)	96·41 (3)	85·58 (1)
γ (°)	–	79·54 (2)
Z	4	2
D_x (Mg m^{-3})	1·16	1·22
Crystal dimensions (mm)	0·5 × 0·25 × 0·15	0·4 × 0·2 × 0·2
Radiation	Mo	Mo
Monochromator	Graphite	Graphite
Scan	ω	ω–2θ
$\Delta\omega$ (°)	1·3 + 0·35 tan θ	1·1 + 0·35 tan θ
Aperture height (mm)	4	4
Aperture width (mm)	1·75 + 1·0 tan θ	1·75 + 1·0 tan θ
Maximum scan speed (deg min^{-1})	10·06	6·75
Prescan acceptance limit	30σ	50σ
Maximum counting time (s)	75	120
Maximum θ (°)	25	25
Number of check reflexions	3	3
Variation of checks (%)	±3	±2
Total reflexions	2219	2104
Reflexions >3σ‡	931 (42%)	1126 (54%)
$|E|$	373 > 1·2	412 > 1·4
$|E|$ statistics	Centrosymmetric	Centrosymmetric
R	0·048	0·070
R_w	0·064	0·082
Goodness of fit	1·75	2·51

* 2,3,4aβ,8aβ-Tetramethyl-4a,5,8,8a-tetrahydro-1-naphthoquin-4β-ol.

† Systematic name: 1β,5β,6β,11β-tetramethyl-3-oxatetracyclo-[5.4.0.0^{2,6}.0^{4,11}]undec-8-en-2β-ol.

‡ $\sigma^2(I) = S + B + (0.04S)^2$, S = scan count, B = background count.

is important in discussing the photochemical reactivity, was well located.

The refinement of the photoproduct structure was somewhat less satisfactory, although the O atoms were easily recognized in the early stages by abnormally low U values when entered as C. The hydrogens were all located on a difference map, but some were poorly defined; refinement gave a negative U value for H(3) and C—H distances of 1·3–1·5 Å for H(3), H(51), H(52), and H(6). These four H atoms were therefore fixed at ideal positions, with U values of 110% of the isotropic equivalent of their bonded C atoms. The final R value was 0·070 (Table 1); mean and maximum shift/error on the final cycle were 0·10 and 1·0, respectively. A final difference synthesis had random fluctuations of up to $\pm$0·3 e Å^{-3}, and one peak of 0·8 e Å^{-3} at (0·61,0·15,0·81); the thermal ellipsoids were generally elongated in the **b** direction (mean values of

Table 2. *Final positional parameters* (*fractional* $\times 10^4$, *for* H $\times 10^3$) *with e.s.d.'s in parentheses*

	Naphthoquinol ($P2_1/n$)				Photoproduct ($P\bar{1}$)		
	x	y	z		x	y	z
C(1)	6635 (5)	3994 (4)	6900 (3)	C(1)	9210 (6)	4478 (7)	6739 (3)
C(2)	5299 (6)	3663 (4)	6166 (3)	C(2)	9258 (7)	2441 (7)	7175 (4)
C(3)	3515 (6)	3932 (4)	6182 (3)	C(3)	7261 (7)	2206 (7)	6784 (4)
C(4)	2824 (5)	4523 (4)	6952 (3)	C(4)	6284 (7)	4200 (7)	6547 (4)
C(4a)	4274 (5)	5182 (4)	7538 (3)	C(4a)	6029 (6)	5027 (7)	7634 (4)
C(5)	3481 (8)	5501 (6)	8390 (4)	C(5)	4834 (9)	4000 (9)	8595 (5)
C(6)	3367 (8)	4423 (7)	8968 (3)	C(6)	5896 (11)	2328 (10)	9381 (5)
C(7)	4185 (7)	3422 (7)	8885 (3)	C(7)	7773 (10)	1864 (9)	9341 (5)
C(8)	5368 (6)	3172 (5)	8184 (3)	C(8)	9025 (8)	2850 (8)	8457 (4)
C(8a)	5969 (5)	4337 (4)	7749 (3)	C(8a)	8220 (6)	4864 (7)	7909 (3)
C(21)	6060 (12)	3051 (9)	5401 (5)	C(21)	11076 (11)	1105 (12)	6921 (8)
C(31)	2095 (12)	3646 (10)	5432 (5)	C(31)	7349 (13)	1330 (12)	5729 (6)
C(41)	4790 (9)	6349 (5)	7097 (5)	C(41)	4972 (10)	6992 (10)	7299 (7)
C(81)	7524 (9)	4928 (9)	8331 (5)	C(81)	8751 (11)	6311 (11)	8426 (6)
O(1)	8286 (4)	3946 (3)	6824 (2)	O(1)	10879 (5)	5195 (6)	6396 (3)
O(4)	1366 (4)	5335 (3)	6659 (2)	O(4)	7763 (4)	5114 (4)	5865 (2)
H(O4)	14 (15)	489 (11)	661 (7)	H(O)	1126 (8)	503 (7)	582 (5)
H(4)	237 (4)	383 (3)	735 (2)	H(3)	658	151	745
H(51)	438 (7)	620 (5)	875 (3)	H(4)	513 (8)	443 (6)	617 (4)
H(52)	194 (10)	572 (5)	800 (4)	H(51)	420	483	907
H(6)	264 (6)	459 (4)	941 (3)	H(52)	379	364	823
H(7)	402 (6)	270 (4)	923 (3)	H(6)	511	154	992
H(81)	652 (6)	272 (4)	846 (3)	H(7)	837 (9)	57 (8)	986 (5)
H(82)	470 (5)	253 (4)	768 (3)	H(81)	1028 (7)	278 (6)	875 (4)
H(211)	627 (12)	358 (9)	492 (7)	H(211)	1110 (8)	127 (8)	611 (5)
H(212)	672 (19)	249 (14)	564 (9)	H(212)	1225 (12)	203 (10)	697 (6)
H(213)	508 (13)	229 (8)	510 (6)	H(213)	1088 (9)	−17 (9)	726 (5)
H(311)	262 (9)	303 (6)	513 (4)	H(311)	792 (10)	0 (10)	587 (6)
H(312)	119 (8)	333 (5)	564 (4)	H(312)	589 (10)	151 (8)	553 (5)
H(313)	196 (11)	443 (8)	531 (5)	H(313)	789 (8)	214 (8)	502 (5)
H(411)	366 (8)	688 (5)	704 (4)	H(411)	492 (9)	762 (8)	779 (5)
H(412)	544 (6)	622 (4)	662 (3)	H(412)	355 (10)	691 (8)	711 (5)
H(413)	556 (8)	680 (6)	744 (4)	H(413)	564 (10)	785 (9)	673 (6)
H(811)	711 (6)	525 (4)	885 (3)	H(811)	851 (10)	752 (10)	802 (6)
H(812)	813 (9)	574 (6)	807 (4)	H(812)	999 (10)	621 (8)	858 (5)
H(813)	812 (10)	428 (7)	862 (5)	H(813)	814 (9)	634 (7)	919 (6)

U_{ii} are 4·7, 8·3, and 5·7 × 10^{-2} Å² for $i = 1, 2$, and 3, respectively). These anomalous features probably result from a small amount of disorder. Apart from C(5) and C(6), the molecule (Fig. 1) has an approximate mirror plane through O(1), C(1), O(4), C(4), C(7), and C(8), and two of the largest peaks on the final difference map (0·8 and 0·3 e Å⁻³) corresponded roughly to the C(5) and C(6) positions reflected in this plane; the initial refined position of H(3) corresponded to the 0·8 e Å⁻³ peak. No attempt was made to allow specifically for the small amount of disorder in the model, since the present description is sufficient to answer the chemical problem.

Final positional parameters for both structures are listed in Table 2.*

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* Lists of structure factors, thermal parameters, bond distances involving hydrogen atoms, torsion angles, and packing diagrams for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35182 (48 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion

Naphthoquinol

The molecule of 2,3,4aβ,8aβ-tetramethyl-4a,5,8,8a-tetrahydro-1-naphthoquin-4β-ol (I) has the same ring-flipped conformation (Fig. 1) as the hexamethyl 4β-ol analogue (Greenhough & Trotter, 1980), such that the hydroxyl group is pseudo-equatorial to the cyclohexenone moiety. The two fused six-membered rings are twisted about the C(4a)–C(8a) bond, with bridgehead torsion angles C(41)–C(4a)–C(8a)–C(81) = 58·1 (5), C(4)–C(4a)–C(8a)–C(8) = −58·3 (4)°; the former angle is 58·6 (2)° in the hexamethyl 4β-ol derivative, and 59·9 (1)° in the hexamethyl 4α-ol compound (which has the alternate ring-flipped conformation). As a consequence of the conformation observed for the present tetramethyl 4β-ol (and for the hexamethyl 4β-ol) there is a close intramolecular non-bonded approach of H(82) to the enone carbon atoms C(2) and C(3), with C(2)···H(82) = 2·74 (4), C(3)···H(82) =

Table 3. Bond distances (Å) and angles (°)

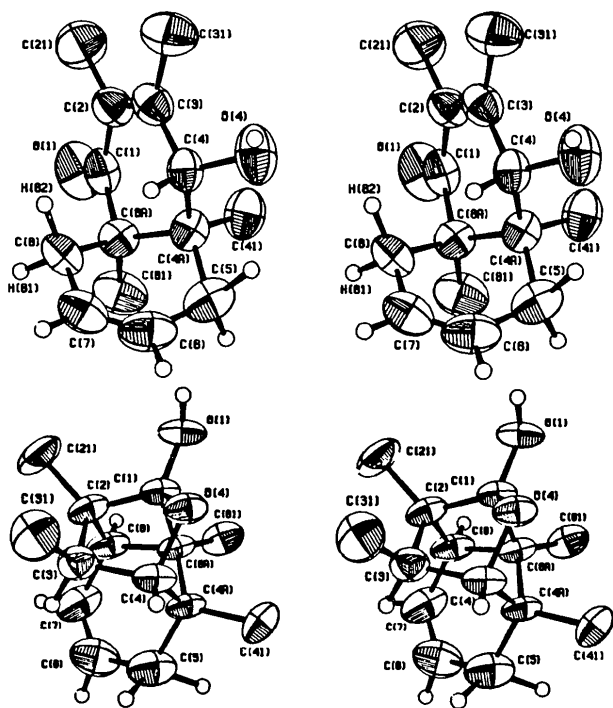|	Naphtho-quinol	Photo-product		Naphtho-quinol	Photo-product		Naphtho-quinol	Photo-product
C(1)—C(2)	1·462 (6)	1·522 (7)	C(8a)—C(1)—C(2)	119·4 (3)	90·5 (3)	C(5)—C(6)—C(7)	125·3 (5)	122·8 (6)
C(2)—C(3)	1·343 (6)	1·554 (7)	C(8a)—C(1)—O(1)	120·9 (4)	115·8 (4)	C(6)—C(7)—C(8)	123·6 (6)	122·1 (5)
C(3)—C(4)	1·500 (5)	1·524 (7)	C(2)—C(1)—O(1)	119·6 (4)	121·9 (4)	C(7)—C(8)—C(8a)	112·2 (5)	117·5 (4)
C(4)—C(4a)	1·509 (5)	1·528 (7)	C(1)—C(2)—C(3)	119·8 (4)	101·3 (4)	C(8)—C(8a)—C(1)	107·7 (4)	87·3 (3)
C(4a)—C(5)	1·543 (6)	1·518 (7)	C(1)—C(2)—C(21)	116·6 (5)	119·3 (5)	C(8)—C(8a)—C(4a)	109·8 (3)	108·9 (4)
C(5)—C(6)	1·506 (8)	1·513 (9)	C(3)—C(2)—C(21)	123·6 (5)	118·5 (5)	C(4a)—C(8a)—C(81)	112·7 (5)	117·4 (4)
C(6)—C(7)	1·280 (8)	1·294 (8)	C(2)—C(3)—C(4)	121·8 (4)	98·8 (4)	C(81)—C(8a)—C(8)	109·5 (5)	118·2 (5)
C(7)—C(8)	1·491 (7)	1·475 (8)	C(2)—C(3)—C(31)	121·8 (5)	115·5 (5)	C(81)—C(8a)—C(1)	109·6 (4)	120·2 (4)
C(8)—C(8a)	1·549 (6)	1·551 (7)	C(4)—C(3)—C(31)	116·3 (5)	113·0 (5)	C(4a)—C(8a)—C(1)	107·3 (3)	100·0 (3)
C(1)—C(8a)	1·504 (6)	1·553 (6)	C(3)—C(4)—C(4a)	114·6 (3)	112·9 (4)	C(2)—C(1)—O(4)	–	107·9 (4)
C(4a)—C(8a)	1·563 (5)	1·565 (6)	C(3)—C(4)—O(4)	109·3 (4)	103·0 (4)	C(8a)—C(1)—O(4)	–	107·3 (3)
C(1)—O(1)	1·228 (4)	1·373 (6)	C(4a)—C(4)—O(4)	109·4 (3)	102·6 (4)	O(1)—C(1)—O(4)	–	111·2 (3)
C(2)—C(21)	1·527 (8)	1·530 (7)	C(4)—C(4a)—C(5)	108·8 (4)	112·2 (5)	C(1)—C(2)—C(8)	–	86·8 (4)
C(3)—C(31)	1·505 (7)	1·523 (8)	C(4)—C(4a)—C(41)	109·6 (4)	108·1 (5)	C(3)—C(2)—C(8)	–	109·9 (4)
C(4)—O(4)	1·433 (5)	1·446 (6)	C(4)—C(4a)—C(8a)	108·7 (3)	99·6 (3)	C(8)—C(2)—C(21)	–	116·0 (5)
C(4a)—C(41)	1·536 (7)	1·528 (8)	C(41)—C(4a)—C(5)	108·7 (5)	108·5 (5)	C(2)—C(8)—C(7)	–	119·7 (5)
C(8a)—C(81)	1·522 (6)	1·481 (8)	C(41)—C(4a)—C(8a)	112·0 (4)	113·7 (5)	C(2)—C(8)—C(8a)	–	88·0 (3)
C(2)—C(8)	–	1·595 (7)	C(5)—C(4a)—C(8a)	109·0 (4)	114·4 (4)	C(1)—O(4)—C(4)	–	94·7 (3)
C(1)—O(4)	–	1·444 (5)	C(4a)—C(5)—C(6)	112·2 (5)	117·4 (5)			

Fig. 1. Stereodiagrams of 2,3,4aβ,8aβ-tetramethyl-4a,5,8,8a-tetrahydro-1-naphthoquin-4β-ol (top) and its solid-state photoproduct (bottom). Thermal ellipsoids are at the 50% probability level and methyl H atoms are omitted for clarity.

2·85 (4) Å [the corresponding distances for the hexamethyl 4β-ol are 2·88 (2) and 2·92 (2) Å, respectively]. The C(2)=C(3) and C(6)=C(7) double bonds are non-parallel and well separated [C(2)···C(7) = 4·393 (7), C(3)···C(6) = 4·369 (7) Å], and there are no C=O···H relationships within the molecule which are geometrically favourable for photoconversion. The

structure of the solid-state photoproduct (see below) indicates that the photon reaction is initiated by H(82) abstraction by the β-enone atom C(3); the geometrical parameters relevant to the abstraction are Δ_c[C(2)—C(3)···H(82)] = 71·6 (8)° and τ_c [angle between the C(3)···H(82) vector and the enone plane defined by Me—C(2)—C(3)—Me] = 50·6°, the corresponding values at C(2) are Δ_c = 80·7 (8), τ_c = 53·4°. The hexamethyl 4β-ol is unreactive in the solid state, although Δ_c and τ_c at C(3) are 75·2 (5) and 49·3°, respectively, and the C(3)···H(82) contact of 2·92 (2) Å is only one and one half e.s.d.'s longer than that of 2·85 (4) Å in the present tetramethyl 4β-ol. The reactive hexamethyl 4α-ol has C(3)···H(52) = 2·72 (2) Å, with Δ_c and τ_c at C(3) of 78·5 (3) and 53·2°, respectively. The reactivity therefore appears to depend critically on the C(3)···H abstraction distance. The present compound contains two close intramolecular H···H contacts, H(52)···H(O4) = 2·57 (12) and H(82)···H(4) = 2·25 (4) Å; H(O4) is poorly defined here, but the latter distance is very similar to the corresponding contact of 2·27 (3) Å in the hexamethyl 4β-ol, suggesting that this contact does not influence the photochemical reactivities.

The photoconversion in solution proceeds via intramolecular 2 + 2 cycloaddition, as for all the derivatives studied (Appel, Greenhough, Scheffer, Trotter & Walsh, 1980), probably due to reaction via higher-energy conformers which fulfil the requirements for this reaction (Greenhough & Trotter, 1980).

The bond lengths and angles in the tetramethyl 4β-ol (Table 3) have normal values which compare well with those in the hexamethyl derivatives. There are differences in torsion angles between the tetramethyl and hexamethyl 4β-ols of up to 10°, e.g. C(8a)—C(1)—C(2)—C(3) = 15·6 (5) and 5·4 (2), C(4a)—C(8a)—C(1)—C(2) = −43·5 (4) and −36·6 (2)°, respectively;

these result in the slightly shorter H(82)···C(2) and C(3) contacts in the present structure. Both six-membered rings have distorted half-chair conformations; C(4a) and C(8a) deviate by -0.45 and $+0.31$ Å from the mean plane of C(1) to C(4), and by $+0.36$ and -0.41 Å from the mean plane of C(5) to C(8) (e.s.d. of deviations $= 0.004$ Å). The carbonyl group is planar to within three standard deviations.

Molecules in the crystal are linked by hydrogen bonds, O(1)···O(4) $= 2.770$ (4) Å, O(4)–H(O4)··· O(1) $= 164$ (9)°, to form chains along **a**. The molecular-packing diagram has been deposited.

Photoproduct

The molecular structure of the polycyclic hemiacetal photoproduct (II) is shown in Fig. 1, where the atom numbering of the parent naphthoquinol (I) is retained. The structures allow the solid-state photoconversion (I) → (II) to be assigned as H abstraction from C(8) by C(3), C(2) to C(8) bonding (I'), and finally cyclization [C(1) to O(4) bonding] to form the hemiacetal (II) (Appel, Greenhough, Scheffer, Trotter & Walsh, 1980).

The six-membered ring, C(4a), C(5), C(6), C(7), C(8), C(8a), is in a flattened half-chair conformation, with C(4a) and C(8a) displaced by $+0.08$ and -0.49 Å, respectively (e.s.d.'s 0.005 Å), from the plane of C(5) to C(8) (in comparison with $+0.36$ and -0.41 Å displacements in the naphthoquinol starting material, see above). The C(1), C(2), C(3), C(4), C(4a), C(8a) ring is a boat, with the oxygen-bridged C(1) and C(4) atoms displaced by 1.07 and 0.75 Å, respectively, from the C(2), C(3), C(4a), C(8a) plane; these four coplanar atoms, C(4), and C(8) form a chair-shaped ring [C(8) displaced by -1.06 Å]. The two hetero-oxygen five-membered rings have envelope conformations with

O(4) displaced 0.750 (3) Å from the C(1), C(2), C(3), C(4) and 0.766 (3) Å from the C(1), C(4), C(4a), C(8a) planes. The four-membered ring is folded; C(8) is 0.55 Å out of the C(1), C(2), C(8a) plane.

The bond lengths and angles (Table 3) in the four-membered ring [formed from the starting material by C(2)–C(8) bonding] are indicative of the strain in the molecule. The internal angles in this ring range from 86.8 (4) to 90.5 (3)°, with C(2)–C(8) $= 1.595$ (7) Å. The angle at the bridging oxygen O(4) is 94.7 (3)°, with other angles in the five-membered hetero-rings ranging from 98.8 (4)° at C(3) to 103.0 (4)° at C(4). In view of the possibility of disorder no significance is attached to minor variations in bond distances and angles from expected values.

Molecules in the crystal are joined into centrosymmetric dimers by pairs of hydrogen bonds, O(1)–H(O)···O(4), with O···O $= 2.801$ (5), O(1)–H(O) $= 0.73$ (6), H(O)···O(4) $= 2.07$ (6) Å, O–H···O $= 173$ (6)°. Distances between dimers correspond to van der Waals interactions.

References

APPEL, W. K., GREENHOUGH, T. J., SCHEFFER, J. R., TROTTER, J. & WALSH, L. (1980). *J. Am. Chem. Soc.* **102**, 1158–1161.
GREENHOUGH, T. J. & TROTTER, J. (1980). *Acta Cryst.* B36, 1831–1835.

The Structures of 1-Oxo-1,2-dihydro-2,3-diazaphenothiazine and 1-Chloro-10-methyl-2,3-diazaphenothiazine

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Abstract

The crystal and molecular structures of 1-oxo-1,2-dihydro-2,3-diazaphenothiazine [space group $P\bar{1}$, $a = 8.00$ (1), $b = 14.03$ (1), $c = 4.36$ (1) Å, $\alpha = 87.7$ (2), $\beta = 101.5$ (2), $\gamma = 101.2$ (3)°] and of 1-chloro-10-methyl-2,3-diazaphenothiazine [space group *Pbca*, $a = 19.83$ (2), $b = 15.29$ (2), $c = 7.32$ (1) Å] have been determined by direct methods and refined by least squares to final residuals R of 0.087 and 0.103