Table 2. *Selected torsion angles (°)*

C1—C2—C3—C4	55.8 (5)	C5—C6—C7—C8	52.5 (5)
C2—C3—C4—C5	−56.5 (5)	C6—C7—C8—C9	−51.9 (5)
C3—C4—C5—C10	56.1 (4)	C7—C8—C9—C10	48.6 (5)
C4—C5—C10—C1	−57.6 (4)	C8—C9—C10—C5	−49.2 (5)
C5—C10—C1—C2	57.3 (5)	C9—C10—C5—C6	47.3 (4)
C10—C1—C2—C3	−55.0 (5)	C10—C5—C6—C7	−47.3 (5)

Data collection: Seifert XRD3000-*S* diffractometer software. Cell refinement: *LSUCRE* (Appleman, 1995). Data reduction: *XRAY*80 (Stewart, 1978). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1992). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1084). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Hydrogen Bonding in 4,4-Dimethylcyclohexane-1,3-dione and 2,5,5-Trimethylcyclohexane-1,3-dione Monohydrate

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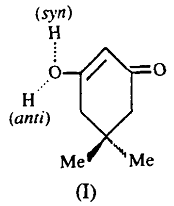
Abstract

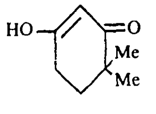
The enol of 4,4-dimethylcyclohexane-1,3-dione (3-hydroxy-6,6-dimethylcyclohex-2-en-1-one, $C_8H_{12}O_2$) forms hydrogen-bonded spiral chains like those in 5,5-dimethylcyclohexane-1,3-dione, except for disorder of the optical isomers. 2,5,5-Trimethylcyclohexane-1,3-dione monohydrate (enol form 3-hydroxy-2,5,5-trimethylcyclohex-2-en-1-one monohydrate, $C_9H_{14}O_2.H_2O$) forms hydrogen-bonded layers containing tetramolecular rings with a short OH···water hydrogen bond [2.428 (4) Å].

Comment

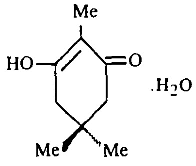
Since cyclohexane-1,3-dione (CHD) and its derivatives are extensively enolized [see (I) below], there are possibilities of >C—O—H···O=C< hydrogen-bonded networks in the solid state. These networks can be involved in supramolecular structures such as the clathrate-like $(\mathrm{CHD})_6$–benzene structure (Etter, Urbanczyck-Lipkowska, Jahn & Frey, 1986) and the dimeric encapsulate $[\mathrm{Cr(C_6H_6)_2^+}.(\mathrm{CHD})_4^-]_2$ (Braga, Grepioni, Bryne & Wolf, 1995). The intermolecular hydrogen bonds in these networks are relatively strong, with O···O distances in the range 2.55–2.60 Å. In practice, the hydroxy proton in CHD derivatives is found close to the idealized *syn* or *anti* positions, indicated in (I) below. Similarly, the sp^2 positions of formal lone pairs of electrons on the



(I)



(II)



(III)

carbonyl O atom suggest hydrogen bonding in the *syn* or *anti* positions. In CHD (Etter, Urbanczyck-Lipkowska, Jahn & Frey, 1986), intermolecular *anti,anti* hydrogen bonds [2.561 (4) Å] give linear chains of molecules related by a glide plane. These are *C*(12) chains in the notation of Etter (1990). In $(CHD)_6$–benzene, *syn,anti* hydrogen bonding [2.579 (1) Å] leads to $R_6^6(36)$ hexameric ring formation, while *syn,syn* hydrogen bonding (2.595 Å) in monoclinic 5,5-dimethylcyclohexane-1,3-dione (dimedone) (Singh & Calvo, 1975) gives *C*(12) spiral chains about a screw axis.

Orthorhombic 4,4-dimethylcyclohexane-1,3-dione, (II) (Fig. 1), contains very similar chains (Fig. 2) to those in dimedone. The repeat distance is 6.699 (2) Å at 150 K, compared with 6.835 (3) Å for room-temperature dimedone. The O···O distance is 2.607 (3) Å.

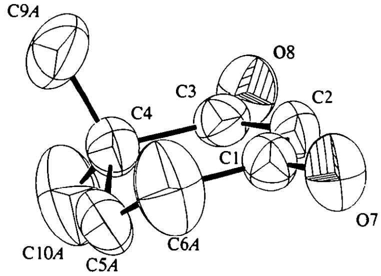


Fig. 1. The structure of 4,4-dimethylcyclohexane-1,3-dione, showing the *A* positions of the disordered C5, C6, C9 and C10 atoms. Displacement ellipsoids are drawn at 50% probability.

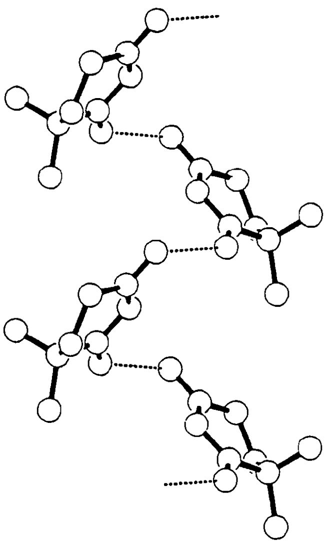


Fig. 2. Spiral chains in 4,4-dimethylcyclohexane-1,3-dione.

Each of these enol CHD derivatives adopts a sofa configuration, with the C5 atom out of the plane of C1, C2, C3, O7 and O8. The molecules are thus chiral. In 5,5-dimethylcyclohexane-1,3-dione, the structure is ordered, with chains of opposite chirality related by the centres of inversion in $P2_1/c$ (Singh & Calvo, 1975). CHD ($P2_1/a$) is disordered with well resolved positions for C5 above and below the molecular plane. Since the glide operation links alternate optical isomers in the chain, the disorder may arise from irregular packing of the chains. Similar disorder is observed in (II) ($P2_12_12_1$), where alternative positions (*A* and *B*) were required for C5 and C6 as well as for the C4 methyl groups C9 and C10. The fractional occupancy of the *A* sites is 0.553 (6), corresponding closely to a racemate crystallizing in a chiral space group. The disorder affects only the outside of the spiral chains. It is not clear whether it should be interpreted as mixed chirality within a spiral or randomly packed spirals with molecules all of one chirality. Attempts to model the disorder as twinning were not successful. Katrusiak (1990) reported that the disorder in CHD is removed at high pressure. Estimates of the barrier to interconversion in an isolated cyclohexane molecule range from 50.4 to 72.6 kJ mol^{-1} (Laane & Choo, 1994)

Crystals of 2,5,5-trimethylcyclohexane-1,3-dione, (III), were found to be hydrated (Fig. 3). In this compound, there is no disorder; hydrogen bonds to water dominate and there are no short inter-dione contacts. The structure is made up of rumpled layers parallel to [012] (Fig. 4). These layers consist of $R_8^8(32)$ rings of four dione molecules alternating with O12 water molecules by way of O7—H71···O12 [O···O 2.428 (4) Å], O12—H121···O8($x-1$, $\frac{1}{2}-y$, $z-\frac{1}{2}$) [O···O 2.716 (4) Å] and O12—H122···O8($1-x$, $\frac{1}{2}+y$, $\frac{3}{2}-z$) [O···O 2.695 (4) Å] hydrogen bonds. Each ring is fused to four symmetry-related rings, creating additional $R_4^4(8)$ rings *via* the O8···O12 hydrogen bonds. The rings are centred at 1,0,$\frac{1}{2}$ [$R_8^8(32)$] and 0,0,0 [$R_4^4(8)$].

Unusually for a 'very short' hydrogen bond (Whitesides *et al.*, 1995), H7 is not located at the centre of the O7···O12 bond [O7—H71 1.167 (4), H71···O12 1.298 (4) Å and O7—H71···O12 160.1 (6)°]. The weaker hydrogen bond to the keto O8 atom in (III)

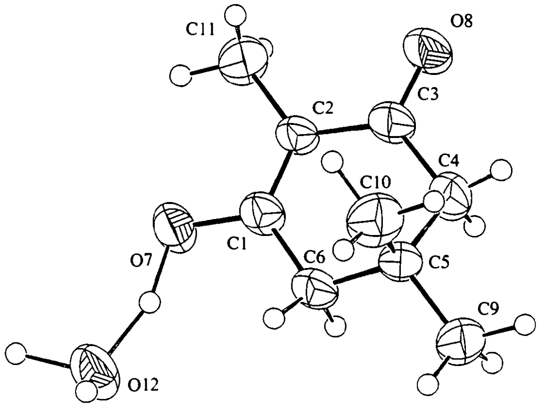


Fig. 3. The enol form of 2,5,5-trimethylcyclohexane-1,3-dione, showing the O21 water molecule. Displacement ellipsoids are drawn at 50% probability.

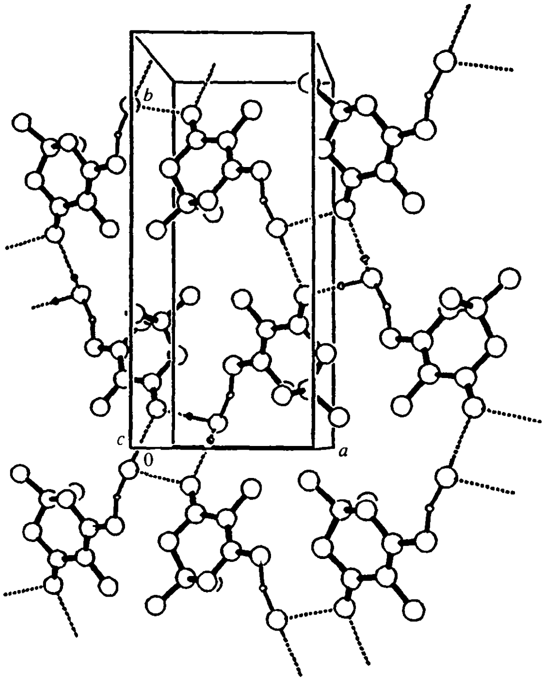


Fig. 4. The hydrogen-bonded layer in 2,5,5-trimethylcyclohexane-1,3-dione, showing the tetramolecular rings.

is reflected in the significant shortening of the C3—O8 distance [1.176 (5) Å] compared with those in (II), CHD and dimedone (average 1.23 Å), whereas the C1—O7 bond length is very similar in these compounds (average 1.3 Å).

No hydrates have been reported for (II), CHD or dimedone. Only 2,5,5-trimethylcyclohexane-1,3-dione can crystallize in this network because the space in the middle of the tetramolecular rings can be filled by the 2-methyl groups of one pair of molecules and the 5,5-dimethyl groups of the other pair. This is somewhat similar to $(\mathrm{CHD})_6$–benzene, with the space-filling role of the benzene taken by the 2,5,5-methyl groups.

These diones are quite reactive; attempts to prepare salts or metal complexes analogous to acetylacetonates have given polymers (Barnes, 1996*a*,*b*)

Experimental

Compound (II) was obtained from Aldrich and used as received. A sample of compound (III) was obtained from Dundee University Laboratory Museum; its origin and date of preparation are unknown.

Compound (II)

Crystal data

$C_8H_{12}O_2$
$M_r = 140.18$
Orthorhombic
$P2_12_12_1$
$a = 6.6990\,(15)$ Å
$b = 9.3743\,(3)$ Å
$c = 12.892\,(4)$ Å
$V = 809.6\,(3)$ Å^3
$Z = 4$
$D_x = 1.150$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 250 reflections
$\mu = 0.081$ mm^{-1}
$T = 293\,(2)$ K
Block
0.4 × 0.2 × 0.2 mm
Colourless

Data collection

Enraf–Nonius CAD-4 FAST system
Area-detector scans
Absorption correction: none
3296 measured reflections
1248 independent reflections

842 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.080$
$\theta_{\rm max} = 24.88°$
$h = -7 \rightarrow 5$
$k = -10 \rightarrow 10$
$l = -14 \rightarrow 12$
Intensity decay: see below

Refinement

Refinement on F^2
$R(F) = 0.0387$
$wR(F^2) = 0.0986$
$S = 0.564$
1247 reflections
132 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.089$
$\Delta\rho_{\rm max} = 0.117$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.118$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (II)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
C1	0.9335 (3)	0.4824 (2)	−0.02680 (15)	0.0607 (5)
C2	1.0307 (3)	0.3618 (2)	−0.05192 (14)	0.0572 (5)
C3	1.1811 (3)	0.3584 (2)	−0.12993 (14)	0.0575 (5)
C4	1.2358 (3)	0.4931 (2)	−0.18741 (14)	0.0633 (5)
C5*A*†	1.1910 (9)	0.6218 (5)	−0.1226 (4)	0.086 (2)
C5*B*‡	1.0521 (9)	0.6024 (5)	−0.1834 (5)	0.078 (2)
C6*A*†	0.9707 (16)	0.6157 (14)	−0.0765 (11)	0.111 (6)
C6*B*‡	0.9822 (20)	0.6231 (10)	−0.0784 (8)	0.071 (5)
O7	0.7928 (2)	0.4903 (2)	0.04589 (12)	0.0826 (5)
O8	1.2696 (2)	0.2462 (2)	−0.15167 (10)	0.0747 (5)
C9*A*†	1.1291 (10)	0.4921 (6)	−0.2871 (4)	0.104 (2)
C9*B*‡	1.4152 (9)	0.5541 (7)	−0.1363 (6)	0.103 (3)
C10*A*†	1.4700 (8)	0.4854 (7)	−0.2098 (6)	0.130 (2)
C10*B*‡	1.2687 (14)	0.4637 (9)	−0.3037 (6)	0.112 (3)

† Site occupancy = 0.552 (6). ‡ Site occupancy = 0.448 (6).

Table 2. *Selected geometric parameters (Å, °) for (II)*

C1—O7	1.331 (2)	C4—C9*B*	1.485 (6)
C1—C2	1.344 (3)	C4—C5*A*	1.498 (5)
C1—C6*A*	1.426 (12)	C4—C10*B*	1.540 (7)
C1—C6*B*	1.512 (10)	C4—C10*A*	1.597 (6)
C2—C3	1.424 (3)	C4—C5*B*	1.602 (6)
C3—O8	1.240 (2)	C5*A*—C6*A*	1.592 (12)
C3—C4	1.510 (3)	C5*B*—C6*B*	1.446 (13)
C4—C9*A*	1.471 (6)		
O7—C1—C2	124.0 (2)	C9*B*—C4—C10*B*	112.6 (5)
O7—C1—C6*A*	113.1 (5)	C3—C4—C10*B*	111.3 (4)
C2—C1—C6*A*	123.0 (5)	C9*A*—C4—C10*A*	108.6 (4)

O7—C1—C6*B*	114.4 (5)	C5*A*—C4—C10*A*	109.6 (4)
C2—C1—C6*B*	121.5 (5)	C3—C4—C10*A*	106.8 (3)
C1—C2—C3	122.1 (2)	C9*B*—C4—C5*B*	111.2 (4)
O8—C3—C2	121.1 (2)	C3—C4—C5*B*	109.4 (2)
O8—C3—C4	118.9 (2)	C10*B*—C4—C5*B*	104.8 (4)
C2—C3—C4	120.0 (2)	C4—C5*A*—C6*A*	111.4 (5)
C9*A*—C4—C5*A*	113.3 (3)	C6*B*—C5*B*—C4	111.4 (6)
C9*A*—C4—C3	107.8 (3)	C1—C6*A*—C5*A*	111.2 (8)
C9*B*—C4—C3	107.5 (3)	C5*B*—C6*B*—C1	111.4 (7)
C5*A*—C4—C3	110.6 (2)		

Compound (III)

Crystal data

$C_9H_{14}O_2.H_2O$
$M_r = 172.22$
Monoclinic
$P2_1/c$
$a = 5.863$ (10) Å
$b = 13.558$ (10) Å
$c = 11.225$ (8) Å
$\beta = 97.80$ (10)°
$V = 884.0$ (18) Å^3
$Z = 4$
$D_x = 1.294$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 13 reflections
$\theta = 3$–17°
$\mu = 0.095$ mm^{-1}
$T = 293$ (2) K
Block
0.5 × 0.3 × 0.2 mm
Colourless

Data collection

Stoe Stadi-2 diffractometer
ω scans
Absorption correction: none
1194 measured reflections
864 independent reflections
668 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.020$

$\theta_{\rm max} = 27.09°$
$h = -7 \rightarrow 6$
$k = 0 \rightarrow 17$
$l = 0 \rightarrow 9$
2 standard reflections monitored every 200 reflections
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0652$
$wR(F^2) = 0.1823$
$S = 1.266$
862 reflections
163 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = -0.042$

$\Delta\rho_{\rm max} = 0.152$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.158$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.025 (10)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (III)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
C1	0.5802 (8)	0.2696 (3)	0.6988 (5)	0.0442 (14)
C2	0.6210 (7)	0.1880 (3)	0.7515 (4)	0.0415 (13)
C3	0.8236 (8)	0.1776 (3)	0.8339 (5)	0.053 (2)
C4	0.9912 (9)	0.2533 (4)	0.8535 (7)	0.059 (2)
C5	0.8836 (7)	0.3474 (3)	0.8407 (4)	0.0444 (14)
C6	0.7308 (8)	0.3498 (4)	0.7201 (5)	0.0487 (14)
O7	0.3944 (5)	0.2793 (3)	0.6179 (3)	0.0593 (12)
O8	0.8691 (6)	0.1041 (2)	0.8874 (4)	0.0680 (14)
C9	1.0684 (10)	0.4193 (4)	0.8417 (7)	0.068 (2)
C10	0.7456 (11)	0.3644 (4)	0.9432 (7)	0.068 (2)
C11	0.4660 (10)	0.1077 (4)	0.7280 (7)	0.059 (2)
O12	0.2797 (7)	0.4354 (3)	0.5220 (4)	0.0678 (14)

Table 4. *Selected geometric parameters (Å, °) for (III)*

C1—C2	1.263 (6)	C3—C4	1.417 (7)
C1—O7	1.327 (6)	C4—C5	1.422 (6)
C1—C6	1.400 (6)	C5—C9	1.456 (7)
C2—C3	1.410 (7)	C5—C10	1.512 (8)
C2—C11	1.420 (6)	C5—C6	1.519 (7)
C3—O8	1.176 (5)		
C2—C1—O7	119.5 (4)	O8—C3—C2	122.1 (4)
C2—C1—C6	121.7 (5)	O8—C3—C4	115.5 (5)
O7—C1—C6	118.7 (4)	C2—C3—C4	122.3 (5)
C1—C2—C3	118.9 (4)	C3—C4—C5	110.2 (4)
C1—C2—C11	120.6 (5)	C4—C5—C6	108.0 (5)
C3—C2—C11	120.4 (5)	C1—C6—C5	114.7 (4)

For (II), an area-detector system was used for data collection. Cell dimensions were refined from 250 reflections selected from two regions 90° apart and 5° wide at $\kappa = 90°$. No conventional diffraction standards were monitored; intensities were compared between detector frames. No decay was noted.

Data collection: *MADNES* (Pflugrath & Messerschmitt, 1991) for (II); Stoe Stadi-2 system for (III). Cell refinement: *MADNES* for (II); local program for (III). Data reduction: *MADNES* for (II); *SHELX*76 (Sheldrick, 1976) for (III). For both compounds, program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *PLATON*92 (Spek, 1992*a*) and *PLUTON*92 (Spek, 1992*b*).

The author thanks the EPSRC and Professor M. Hursthouse for the data collection for compound (II).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: LI1150). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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