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3,3,6,6-Tetramethyl-1,2,4,5-tetroxane: a twinned crystal structure

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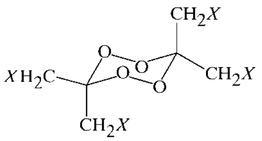
The title compound, $C_6H_{12}O_4$, also known as dimeric acetone peroxide, $Me_2(C_2O_4)Me_2$, has crystallographically imposed inversion symmetry and adopts a chair conformation in the solid state. This structure contrasts with that of the sulfur homologue $Me_2(C_2S_4)Me_2$, which has crystallographically imposed $\overline{4}$ symmetry and crystallizes in a twist-boat conformation. Crystals of the title compound are twinned along the reciprocal c^* axis.

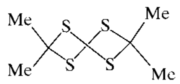
Comment

Because of the particular reactivity of the O—O bond, the synthesis and reactivity of cyclic peroxides have attracted many investigators (Schulz, 2000). Cyclic diperoxides have been used as efficient sources of radicals for the initiation of radical polymerization (Lockley *et al.*, 2000), and the role of cyclic peroxides in the biosynthesis of prostacyclines and thromboxanes is well documented (van Dorp, 1979). Appropriately substituted 1,2,4-trioxanes and 1,2,4,5-tetroxanes display significant antimalarial activities (Jefford *et al.*, 2000). As part of our general interest in cyclic peroxides and heterocyclic hydroperoxides, we have investigated the solid-state structure of 3,3,6,6-tetramethyl-1,2,4,5-tetroxane (or dimeric acetone peroxide), (I). Several thermochemical (Murray *et al.*, 1966; Wulz *et al.*, 1970; Canizo & Cafferta, 1992) and quantum-chemical (Diez & Jubert, 2000) data sets for (I) are available. Solvent effects on the inversion barrier of (I) have been studied (Aganov *et al.*, 1970; Brune *et al.*, 1971), and a conformational analysis in the liquid phase suggested that the chair conformer is more stable than the twist form (Murray *et al.*, 1966; Aganov *et al.*, 1970)

Although (I) has been known for more than 100 years, the crystal structure has not been reported to date. This situation is surprising given the great interest in this compound. In an initial attempt, Groth (1967*a*) reported structures of several dimeric peroxides, but (I) was left undetermined because of a twinning problem. On the other hand, the crystal structure of the similar compound dimeric 1,3-dibromoacetone peroxide, (II) (Schulz *et al.*, 1967), and the sulfur homologue 3,3,6,6-tetramethyl-*S*-tetrathione, $Me_2(C_2S_4)Me_2$, (IV) (Korp *et al.*, 1981), are well known. The aim of the present work was to provide a complete structural analysis of (I), in order to support the findings obtained from density-functional theory, molecular-dynamics calculations and spectroscopic measurements.



(I) X=H
(II) X=Br
(III) X=–(CH$_2$)$_3$



(IV)

Our analysis shows that (I) is located on an inversion centre (Fig. 1), with the chair conformation that was found to be the stable conformer (Murray *et al.*, 1966; Aganov *et al.*, 1970; Diez & Jubert, 2000). Selected geometric parameters are given in Table 1, while complete crystallographic data are available as supplementary material. It is of interest to note that (IV) crystallizes in a twist-boat conformation (Korp *et al.*, 1981), with crystallographically imposed $\overline{4}$ symmetry.

The observed O—O and C—C distances differ only slightly from the calculated values (1.46 and 1.53 Å, respectively), while the measured and calculated (1.43 Å) C—O distances are nearly identical (Diez & Jubert, 2000). However, the 'experimental' values for acetone peroxide discussed by Diez & Jubert (2000) are actually values reported for dimeric cyclohexanone peroxide, (III) (Groth, 1967*a*), and not dimeric acetone peroxide.

The observed C1—O1—O2^{i}, O2—C1—C2, O1—C1—C3 and C3—C1—C2 angles [Table 1; symmetry code: (i) $1 - x$, $1 - y$, $2 - z$] are close to the calculated values (107.9, 112.5, 104.5 and 114.0°, respectively; Diez & Jubert, 2000). Interestingly, the O—O and C—O bond lengths, the C—O—O angle and the C1—O1—O2^{i}—C2^{i} torsion angle differ significantly from the corresponding values for (II) (1.45 and 1.46 Å,

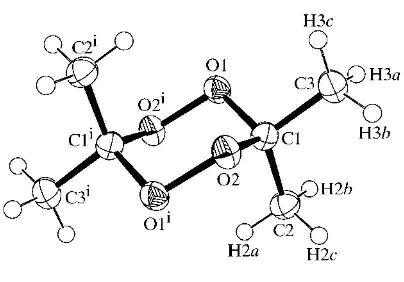


Figure 1
The structure of the dimeric acetone peroxide molecule (displacement ellipsoids are shown at the 50% probability level), including the atom-numbering scheme. [Symmetry code: (i) $-x + 1$, $-y + 1$, $-z + 2$.]

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‡ Responsible for X-ray structure determination and twinning solution.

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and 110 and 61°, respectively; Schulz *et al.*, 1967) but lie in the typical range for dialkyl peroxides and other cyclic peroxides (Matsugo & Saito, 1992). The geometry around atom C1 is a distorted tetrahedron, possibly as a result of an intramolecular repulsive $C-H\cdots O$ interaction (Groth, 1967*a*).

The problem with earlier X-ray investigations of (I) has been the twinning of crystals (Groth, 1967*a*). If, for example, two different orientations of a molecule in a crystal lattice are energetically nearly equivalent, very often a symmetry change can be observed, and sometimes it is not possible to prevent twinning even under idealized conditions, *e.g.* low temperature, slow crystal growth, crystallization from different solvents *etc.*

In Fig. 2(*a*), a general view of the unit cell of (I) is presented, while Fig. 2(*b*) shows a perspective view along [001], clarifying packing effects and the local symmetry environment.

For our three-component twin, the twin rotation tool in *GEMINI* (Sparks, 2000) revealed integer indices in the reciprocal space around [001], the c^* axis vertical to the c face of the crystal. The rotation angles are very close to 180 and 90° for the two additional crystal components (Fig. 3). Using just X-ray data, it is impossible to distinguish between reflection twinning and twofold rotation twinning. However, with the data of the major crystal component, it was possible to determine the space group and to solve the structure, thus enabling us to speculate about the nature of the twinning phenomenon.

A graphical analysis of the twin interface is shown in Fig. 3. For a rotation of 180°, the twin interface can better be described as a mirror plane, because (I) was found to crystallize in a centrosymmetric space group. Interestingly, the structure of 3,6-diphenyl-1,2,4,5-tetraoxacyclohexane was also found to crystallize as a twin with this relatively common (001) plane (Groth, 1967*b*). In both cases (90 and 180° rotation around the c^* axis), the two axial (C2 and C2^{i}) and two equatorial (C3 and C3^{i}) methyl atoms of the chair-shaped acetone peroxide have a local environment that is nearly the same as that of every other molecule in the lattice. These methyl atoms always point towards the centre of the $O1-O2^{i}$ or $O2-O1^{i}$ bridge of the neighbouring molecules. This fact is easily derived from the packing diagram (Fig. 2*b*), viewed along [001]. As a result of this comparable symmetry environment, the total energy of a twinned crystal should be very close to that of a pure untwined sample. Obviously, this would be the reason for the high affinity of (I) for crystallizing as a multiple twin.

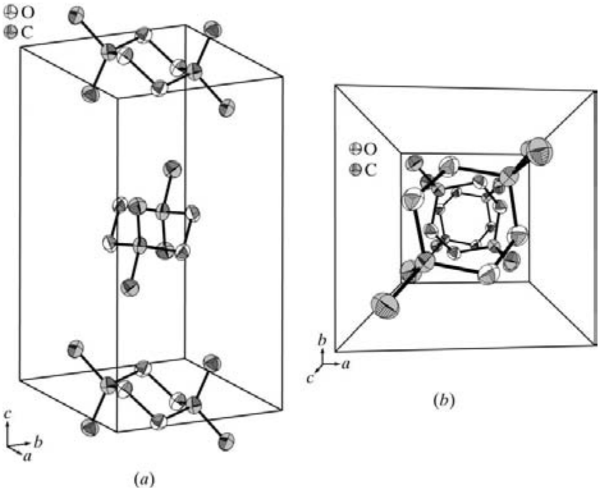

Figure 2
(*a*) A packing diagram of (I). (*b*) A perspective view of the unit cell of (I) along [001], clarifying the packing and the effect of the *c*-glide plane.

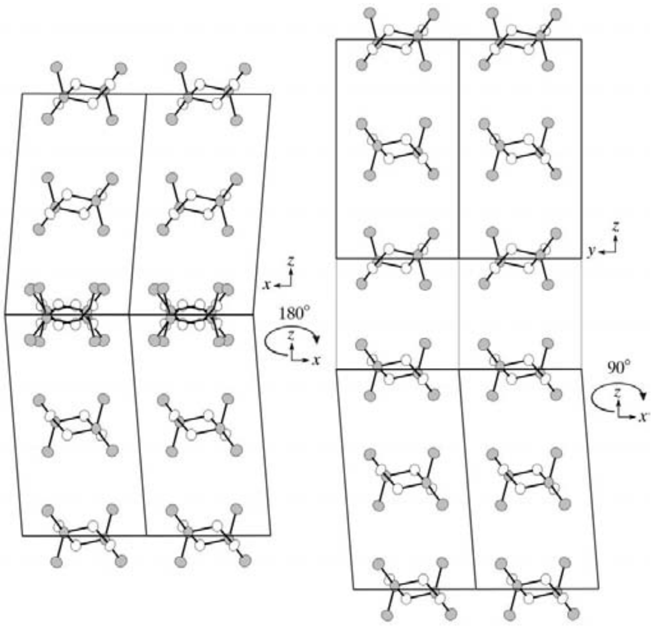

Figure 3
An illustration of the twinning phenomenon along c^*.

Experimental

Compound (I) is potentially an explosive solid and the recommended safety precautions should be taken into account before attempting to prepare it (Dankowski & Prescher, 1988). Since Baeyer & Villiger (1899, 1900) prepared (I) by the treatment of acetone with Caro's acid (peroxomonosulfuric acid, H_2SO_5), many other methods have been developed to synthesize this molecule, including ozonolysis of tetramethylethylene (Criegee, 1953), treatment of acetone with concentrated H_2O_2 in acetonitrile acidified with H_2SO_4 (McCullough *et al.*, 1980) or reaction of acetone with bis(trimethylsilyl) peroxide (Jefford & Boukouvalas, 1988). Compound (I) was prepared in a pure form according to the method described by McCullough *et al.* (1980). No traces of trimeric acetone peroxide were detected by ^{1}H and ^{13}C NMR spectroscopy (Dong & Vennerstrom, 2001). The compound was recrystallized from acetone, yielding clear colourless crystals suitable for structural analysis.

Crystal data

$C_6H_{12}O_4$
$M_r = 148.16$
Monoclinic, $P2/c$
$a = 5.9194\ (8)$ Å
$b = 5.9245\ (8)$ Å
$c = 10.5821\ (14)$ Å
$\beta = 94.326\ (3)°$
$V = 370.05\ (9)$ Å^3
$Z = 2$

$D_x = 1.33$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1547 reflections
$\theta = 3.4–31.3°$
$\mu = 0.11$ mm^{-1}
$T = 208\ (2)$ K
Prism, colourless
0.4 × 0.1 × 0.1 mm

Acta Cryst. (2004). C**60**, o180–o182 Feyissa Gadissa Gelalcha *et al.* • $C_6H_{12}O_4$ **o181**

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
2651 measured reflections
919 independent reflections
764 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.037$
$\theta_{\rm max} = 28.3°$
$h = -7 \rightarrow 7$
$k = -5 \rightarrow 7$
$l = -14 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.113$
$S = 1.11$
919 reflections
70 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0481P)^2 + 0.1358P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.31$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.22$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.4329 (17)	C1—C2	1.518 (2)
O1—O2$^{\rm i}$	1.4753 (14)	C1—C3	1.513 (2)
O2—C1	1.4361 (18)		
C1—O1—O2$^{\rm i}$	107.58 (9)	O1—C1—C3	104.74 (11)
C1—O2—O1$^{\rm i}$	107.31 (10)	O2—C1—C2	112.91 (12)
O1—C1—O2	107.60 (11)	O2—C1—C3	104.54 (12)
O1—C1—C2	112.89 (12)	C3—C1—C2	113.45 (13)
O2$^{\rm i}$—O1—C1—O2	−64.66 (13)	O1$^{\rm i}$—O2—C1—C3	175.46 (10)
O2$^{\rm i}$—O1—C1—C3	−175.50 (11)	O1$^{\rm i}$—O2—C1—C2	−60.76 (14)
O2$^{\rm i}$—O1—C1—C2	60.60 (15)	C1—O1—O2$^{\rm i}$—C1$^{\rm i}$	64.47 (13)
O1$^{\rm i}$—O2—C1—O1	64.48 (12)		

Symmetry code: (i) $1 - x, 1 - y, 2 - z$.

We analysed several samples and, in agreement with earlier investigations (Groth, 1967*a*), were unable to find pure untwinned crystals. Many reflections showed a typical splitting, and the conventional auto-indexing routine in *SMART* (Siemens, 1993) failed to find a plausible unit cell. However, a twin analysis of nearly 1000 reflections with the program *GEMINI* (Sparks, 2000) revealed multiple twinning with at least three different crystal components for our sample. Polysynthetic or multiple twinning usually occurs with perpendicularly twinned crystals, where all of the twin interfaces are parallel to one another. The program *GEMINI* (Sparks, 2000) was used to generate a HKLF-5 file, including reflections of all three components, for refinement with *SHELXL*97 (Sheldrick, 1997). Although it was possible to solve the structure and to find all H atoms, the quality of the structure parameters was still relatively poor. For non-merohedral twins, some reflections exactly overlap, some partially overlap and others do not overlap at all. The relatively poor data quality arises because the integration program *SAINT-Plus* (Bruker, 1999) was not designed to integrate partially overlapped reflections accurately. In addition, it was impossible to obtain an orientation matrix with reasonable accuracy for the third minor component. For these reasons, we isolated the predominant component for an additional experiment. In this case, it was possible to obtain a substantial number of pure reflections from the major component only and the structure could be solved by traditional methods. All structure parameters given in this paper were obtained from this experiment. H-atom coordinates and $U_{\rm iso}$ values were refined; the C—H distances are in the range 0.93 (2)–0.99 (2) Å.

Data collection: *SMART* (Siemens, 1993); cell refinement: *SAINT-Plus* (Bruker, 1999) and *GEMINI* (Sparks, 2000); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1722). Services for accessing these data are described at the back of the journal.

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o182 Feyissa Gadissa Gelalcha *et al.* • $C_6H_{12}O_4$ *Acta Cryst.* (2004). C**60**, o180–o182