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(*E*)-3,5-Dichloro-3,5-bis(chloromethyl)-1,2,4-trioxolane

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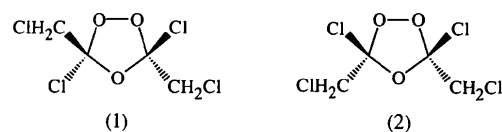
Abstract

The major crystalline product derived from the ozonolysis of 1,2,3,4-tetrachlorobut-2-ene has been shown to be the monocyclic ozonide title compound, C₄H₄Cl₄O₃, (1), rather than the *Z* stereoisomer originally reported. The ozonide ring of (1) adopts a half-chair conformation. The molecules pack together to form sheets linked together by a series of Cl···Cl interactions.

Comment

Recently one of us has reported the first synthesis of stable ozonides derived from acyclic olefins bearing Cl atoms at the C=C double bond (Griesbaum, Schlindwein & Hilß, 1993). Ozonolysis of a solution of (*E*)-1,2,3,4-tetrachlorobut-2-ene in pentane at 233 K afforded a mixture (3:1) of two stereoisomeric ozonides which were separable by column chromatography. On the basis of the published observation that *Z* ozonides have the longer retention time in gas or column chromatography as compared with the corresponding *E* isomers (Bailey, 1978), the minor and major components have been tentatively assigned the *E* and *Z* configurations, respectively, as depicted in structural formulae (1) and (2). Since the results of subsequent HPLC analyses and substitution reactions involving isomers (1) and (2) were inconsistent, it became evident that the use of chromatographic retention times was an unreliable basis for the stereochemical assignment of the isomeric

ozonides (1) and (2). An X-ray crystallographic analysis of the crystalline major component, the supposed *Z* isomer, was undertaken to resolve the structural ambiguity.



From the crystal structure determination it is clear that the tetrachloroozonide corresponding to the major component is in fact the *E* isomer, (1) (Fig. 1), contrary to the previous assignment. The title compound, (1), crystallizes with no crystallographically imposed symmetry. There is a network of significantly short Cl···Cl intermolecular contacts in the range 3.303–3.820 Å such that the molecules of (1) form infinite sheets. The shortest contacts were for Cl1···Cl1ⁱ [3.303 (2) Å; symmetry code: (i) $-x, -y, 1-z$] and Cl2···Cl3ⁱⁱ [3.364 (1) Å; symmetry code: (ii) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$]. An analysis of Cl···Cl intermolecular contacts between 3.0 and 3.4 Å, where both Cl atoms are attached to C atoms, found in the Cambridge Structural Database (CSD) (Fletcher, McMeeking & Parkin, 1996; Allen & Kennard, 1993), indicates that the most frequent distance was between 3.374 and 3.384 Å (65 examples out of a total sample of 530).

The central 1,2,4-trioxolane ring of (1) adopts a half-chair conformation with approximate C₂ symmetry in which the peroxidic O1 and O2 atoms are located on either side of the plane defined by C1, O3 and C2, with the ring Cl atoms and the chloromethyl groups in pseudo-axial and equatorial positions, respectively. This conformation is quite different from that observed for the relatively few examples of monocyclic ozonides found in the CSD (Fletcher, McMeeking & Parkin,

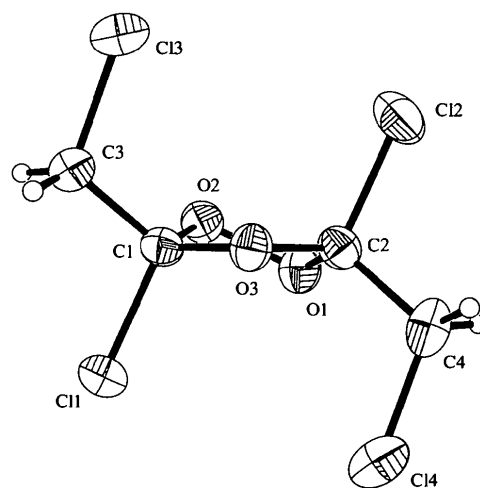


Fig. 1. Perspective view of the molecular structure of the title ozonide with 40% probability displacement ellipsoids, except for H atoms which have artificial radii of 0.1 Å for clarity.

1996; Allen & Kennard, 1993), since the ozonide ring in each of these other cases appeared to favour an alternative envelope conformation with one of the peroxidic O atoms displaced out of the O—C—O—C plane (see Griesbaum *et al.*, 1989; Griesbaum, Krieger-Beck & Beck, 1991; Giordano & Cremola, 1990).

Although the O—O bond length [1.465 (3) Å] is within the expected range (Dunitz, 1979), the remaining C—O bond distances around the 1,2,4-trioxolane ring appear to be significantly shorter than those in other ozonide systems (Griesbaum *et al.*, 1989; Griesbaum, Krieger-Beck & Beck, 1991; Giordano & Cremola, 1990). Bond angles deviate substantially from an idealized tetrahedral geometry in a manner comparable with other five-membered cyclic peroxide systems. The C—Cl bond distances for the ring Cl atoms are significantly longer than those in the chloromethyl groups, consistent with repulsive interactions between these Cl atoms and the neighbouring ring O atoms. The pattern of variation in the C—O and C—Cl bond lengths together with the orientation of the Cl atoms suggest that the overall molecular geometry is determined by an anomeric effect; analogous structural variations have also been observed in the solid state for *cis*-2,3-dichloro-1,4-dioxane (Altona & Romers, 1963). Adjacent Cl atoms adopt an antiperiplanar arrangement [Cl1—C1—C3—Cl3 176.2 (2) and Cl2—C2—C4—Cl4 174.9 (2)°] as a consequence of a combination of intramolecular steric and dipole–dipole interactions and crystal-packing forces. In contrast, the results of molecular mechanics calculations (*MACROMODEL*; Still, 1993) on this system tend to favour synclinal arrangements for these pairs of neighbouring Cl atoms.

Experimental

The ozonization of a solution of 1,2,3,4-tetrachlorobut-2-ene (2.90 g, 15.1 mmol) in pentane (750 ml) at 233 K afforded a mixture of two isomeric ozonides (Griesbaum, Schlindwein & Hilß, 1993). The title compound was isolated by fractional recrystallization of the mixture from dichloromethane/pentane (2:98) at 253 K. Single crystals of (1) suitable for X-ray analysis were obtained by further recrystallization from dichloromethane/pentane (2:98) at 253 K.

Crystal data

C₄H₄Cl₄O₃

M_r = 241.87

Monoclinic

*P*2₁/*c*

a = 10.732 (2) Å

b = 8.9450 (10) Å

c = 10.1450 (10) Å

β = 115.810 (10)°

V = 876.7 (2) Å³

Z = 4

D_x = 1.832 Mg m⁻³

D_m not measured

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 11 reflections

θ = 12.15–12.49°

μ = 1.304 mm⁻¹

T = 293 (2) K

Block

0.57 × 0.35 × 0.35 mm

Colourless

Data collection

Siemens *P4* diffractometer

ω scans

Absorption correction:

empirical via ψ scans

(*XSCANS*: Siemens, 1994)

T_{min} = 0.570, *T_{max}* = 0.634

2884 measured reflections

1235 independent reflections

995 reflections with

I > 2σ(*I*)

R_{int} = 0.035

θ_{max} = 25°

h = -12 → 11

k = -10 → 1

l = -1 → 9

3 standard reflections

every 97 reflections

intensity decay: 8.4%

Refinement

Refinement on *F*²

R[*F*² > 2σ(*F*²)] = 0.036

wR(*F*²) = 0.095

S = 1.061

1235 reflections

100 parameters

H atoms riding; see below

w = 1/[σ²(*F_o*²) + (0.0455*P*)² + 0.4456*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} < 0.001

Δρ_{max} = 0.268 e Å⁻³

Δρ_{min} = -0.240 e Å⁻³

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Cl1—C1	1.798 (3)	O2—C1	1.390 (4)
Cl2—C2	1.807 (4)	O3—C2	1.392 (4)
Cl3—C3	1.760 (4)	O3—C1	1.396 (3)
Cl4—C4	1.755 (4)	C1—C3	1.510 (4)
O1—C2	1.391 (4)	C2—C4	1.518 (4)
O1—O2	1.465 (3)		
C2—O1—O2	101.1 (2)	O1—C2—O3	106.4 (2)
C1—O2—O1	101.7 (2)	O1—C2—C4	110.2 (3)
C2—O3—C1	107.0 (2)	O3—C2—C4	114.1 (3)
O2—C1—O3	105.8 (3)	O1—C2—Cl2	110.4 (3)
O2—C1—C3	110.7 (3)	O3—C2—Cl2	108.9 (2)
O3—C1—C3	114.1 (2)	C4—C2—Cl2	106.8 (2)
O2—C1—Cl1	110.6 (2)	C1—C3—Cl3	111.8 (3)
O3—C1—Cl1	109.5 (2)	C2—C4—Cl4	112.0 (3)
C3—C1—Cl1	106.2 (3)		
Cl1—C1—C3—Cl3	176.2 (2)	Cl2—C2—C4—Cl4	174.9 (2)

H atoms attached to C atoms were located from Δρ but were constrained to idealized positions (C—H 0.97 Å) with *U*_{iso}(H) = 1.5*U*_{eq}(C).

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL/PC*. Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

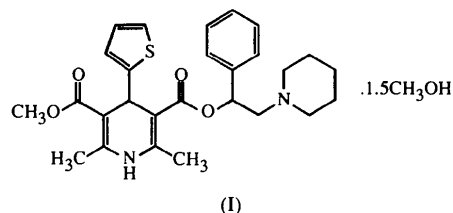
The authors thank Heriot–Watt University for provision of a postdoctoral fellowship (GMR). The use of the EPSRC's Chemical Database Service at CCLRC Daresbury Laboratory is gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1150). Services for accessing these data are described at the back of the journal.

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(Araki, Ao, Inui & Aihara, 1983). The structure analysis has been undertaken in order to confirm the relative configuration of the two chiral centers and to understand the three-dimensional structure.

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(4*RS*,1'*RS*)-Methyl 1-Phenyl-2-piperidinoethyl 1,4-Dihydro-2,6-dimethyl-4-(2-thienyl)pyridine-3,5-dicarboxylate Methanol Solvate, C₂₇H₃₂N₂O₄S.1.5CH₄O

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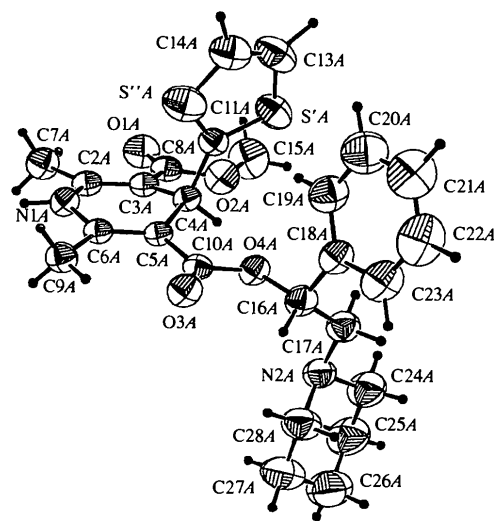
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Abstract

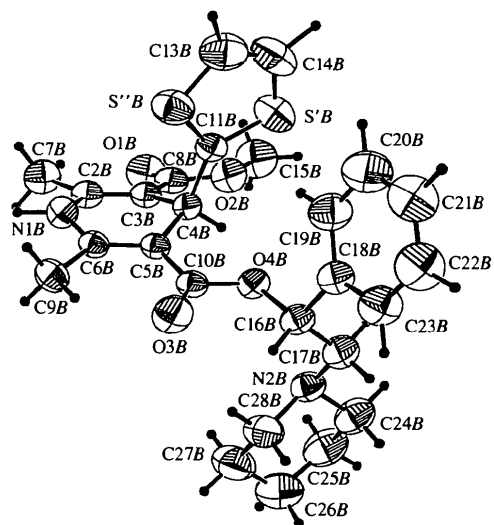
The two independent molecules in the asymmetric unit have similar conformations. The 4-thienyl-1,4-dihydropyridine moieties adopt a flat boat conformation commonly observed for 4-aryl-1,4-dihydropyridine derivatives with the 4-thienyl group in a pseudo-axial orientation. The thienyl and phenyl rings are perpendicular to each other. The six methanol molecules in the unit cell stabilize the crystal structure through intermolecular hydrogen bonds involving the N atoms of the dihydropyridine and the piperidine rings of both molecules.

Comment

Many 1,4-dihydropyridine derivatives are well known as belonging to the most potent class of calcium channel antagonists. In the course of the development of effective antagonists, the title compound, (I), was synthesized



Molecule A



Molecule B

Fig. 1. The molecular structures showing 50% probability displacement ellipsoids (ORTEP; Johnson, 1976).