Crystal structure of 5-oxatricyclo[5.1.0.0^{1,3}]octane-4-one: two polymorphs in one crystal

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Two subsets of data, corresponding to different crystalline modifications of the title compound, 5-oxatricyclo[5.1.0.0^{1,3}]-octane-4-one ($C_7H_8O_2$), have been obtained from the same experiment. Both structures were successfully solved and refined. The packing of identical layers of molecules is different for monoclinic and orthorhombic forms.

1. Introduction

One of the possible routes towards the synthesis of a new class of enantiomeric compounds, [n]triangulanes (de Meijere & Kozhushkov, 2000; de Meijere *et al.*, 2002), starts from *syn*-1,3-disubstituted spiropentane derivatives. Exploring this approach, we have synthesized tricyclic lactone (1). The structural chemistry of the smallest triangulane-spiropentane

(1)
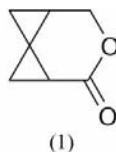
and its derivatives are well studied experimentally and theoretically (Boese, 1992; Boese *et al.*, 1989; Wiberg & Snoonian, 1998). However, to the best of our knowledge, the small molecule (1) is the first structurally studied bridged spiropentane containing a three-membered bridge. The deviation of the spiropentane system of molecule (1) from the ideal C_{2v}-symmetry should be less pronounced than in the case of spiropentanes with two-membered bridges owing to less strain in (1). The X-ray study of (1) was supposed to determine the structure and conformation of the molecule and confirm the predicted geometry. However, the structure determination of (1) turned out to be far from straightforward. It appears from our study that compound (1) forms composite crystals, which is highly unusual for organic compounds.

2. Experimental

The synthesis of (1) and the crystallization procedure have been reported previously (de Meijere *et al.*, 2002). A transparent colourless plate-shaped crystal with dimensions of $0.48 \times 0.34 \times 0.16$ mm was mounted on a glass fibre with perfluorinated oil and placed in a Bruker SMART CCD 1 K diffractometer under a stream of cold nitrogen gas from an Oxford Cryostream low-temperature device. Preliminary data collection yielded a set of 103 reflections, and the indexing procedure (with subsequent least-square refinement of the cell using 101 reflections) resulted in orthorhombic unit-cell

parameters $a = 8.176$ (3), $b = 9.967$ (4), $c = 29.74$ (1) Å and $\alpha = 90.08$ (4), $\beta = 90.05$ (5), $\gamma = 90.05$ (3)°. No abnormal (wide, split *etc.*) reflections were noticed during the visual inspection of the collected frames and all the observed reflections corresponded well to the predicted positions. The full sphere of data was collected at 110.0 (2) K with 7 s exposure per 0.3° ω-scan frame, using graphite monochromated Mo $K\alpha$ radiation. In total, 2050 frames have been collected. The integration (*SAINT*; Bruker, 1998) yielded 26 526 reflections; unrestricted cell refinement using 6637 reflections with $4.3 \le 2\Theta \le 59.8°$ gave metrically orthorhombic unit-cell parameters $a = 8.1852$ (5), $b = 9.9591$ (6), $c = 29.688$ (2) Å and $\alpha = 90.023$ (2), $\beta = 89.992$ (2), $\gamma = 89.991$ (2)°. The data reduction using *XPREP* (Bruker, 1997) unexpectedly gave a much better R_{int} value for transformed $(-b, -a, c)$ monoclinic equivalents than that for orthorhombic ones (0.047 and 0.374, respectively). Observed reflection conditions corresponded to a twofold screw axis along the monoclinic axis and therefore to the $P2_1$ or $P2_1/m$ space group; the centrosymmetric statistics suggested the latter. However, all attempts to obtain a sensible structure solution in the $P2_1/m$ space group as well as in the orthorhombic system failed. The structure was solved in $P2_1$ with eight independent molecules in the unit cell, but the model could not be refined. Careful examination of the original diffraction pattern revealed a rather unusual intensity distribution: among the reflections with $L \ne 4n$, only those with $H = L + 4n$ were the observed ones (Fig. 1). This distribution can be described by the overlapping of two lattices, A and B, with common layers at $H = 4n$. The A lattice is orthorhombic and the B lattice is monoclinic. In order to examine this option, we used the simplest approach: the data were repro-
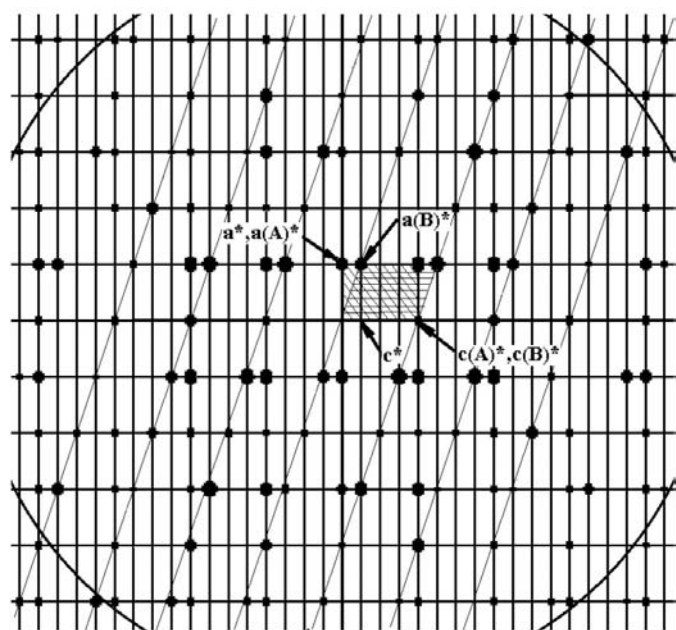

Figure 1
Fragment of reciprocal space plot (*XPREP*) of $H0L$ layer. The rectangular grid shows an original cell setting ($+h$ up, $+l$ to right); letters in brackets indicate the parameters of A and B cells, respectively; the size of the dark spots corresponds to the intensity of the reflections.

Table 1
Experimental details.

	A	B
Crystal data		
Chemical formula	$C_7H_8O_2$	$C_7H_8O_2$
Chemical formula weight	124.13	124.13
Cell setting, space group	Orthorhombic, $P2_12_12_1$	Monoclinic, $P2_1/c$
a, b, c (Å)	9.9644 (8), 8.1854 (7), 7.4422 (6)	9.9533 (8), 8.1831 (7), 7.8129 (6)
β (°)	90	108.61 (2)
V (Å^3)	607.01 (9)	603.06 (8)
Z	4	4
D_x (Mg m^{-3})	1.358	1.367
Radiation type	Mo $K\alpha$	Mo $K\alpha$
No. of reflections for cell parameters	4038	3630
θ range (°)	2.25–30.05	2.61–30.1
μ (mm^{-1})	0.099	0.100
F(000)	264	264
Temperature (K)	110.0 (2)	110.0 (2)
Crystal form, colour	Plate, colourless	Plate, colourless
Crystal size (mm)	$0.48 \times 0.34 \times 0.16$	$0.48 \times 0.34 \times 0.16$
Data collection		
Diffractometer	Bruker *SMART* CCD 1 K	Bruker *SMART* CCD 1 K
Data collection method	ω scans	ω scans
No. of measured, independent and observed reflections	4859, 1266, 1166	4733, 1264, 1061
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.0487	0.0426
θ_{max} (°)	30.24	30.18
Range of h, k, l	$-13 \rightarrow h \rightarrow 13$	$-13 \rightarrow h \rightarrow 13$
	$-11 \rightarrow k \rightarrow 11$	$-11 \rightarrow k \rightarrow 11$
	$-10 \rightarrow l \rightarrow 10$	$-10 \rightarrow l \rightarrow 10$
Absorption correction	None	None
Refinement		
Refinement on	F^2	F^2
$R[F^2>2\sigma(F^2)]$, $wR(F^2)$, S	0.0373, 0.089, 1.169	0.0467, 0.1263, 1.601
No. of reflections and parameters used in refinement	1266, 114	1264, 114
H-atom treatment	All H-atom parameters refined	All H-atom parameters refined
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.05P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.05P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.000	0.000
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.163, −0.145	0.327, −0.179

Computer programs used: *SMART* (Bruker, 1998), *SAINT* (Bruker, 1998), *SHELXTL* (Bruker, 1997).

cessed from the very beginning, using separate orientation matrices corresponding to A and B settings. Two data subsets were obtained. In both cases, the structures were solved without problems. Refinement of the structures without reflections of overlapping layers ($H = 4n$) gave remarkably good results, which are listed in Table 1.

Meanwhile, a sample of (1) has been examined again in order to confirm the results. This examination found a number

Table 2
Selected bond lengths (Å) and angles (°).

Bond	A	B	Bond	A	B
O(1)—C(7)	1.208 (2)	1.218 (2)	C(2)—C(5)	1.484 (2)	1.479 (2)
O(2)—C(7)	1.351 (2)	1.343 (2)	C(3)—C(5)	1.477 (2)	1.479 (2)
O(2)—C(6)	1.482 (2)	1.487 (2)	C(3)—C(7)	1.493 (2)	1.498 (2)
C(1)—C(5)	1.486 (2)	1.480 (2)	C(3)—C(4)	1.555 (2)	1.553 (2)
C(1)—C(6)	1.499 (2)	1.497 (2)	C(4)—C(5)	1.469 (2)	1.479 (2)
C(1)—C(2)	1.543 (2)	1.540 (2)			

Angle	A	B	Angle	A	B
C(7)—O(2)—C(6)	119.2 (1)	118.7 (1)	C(4)—C(5)—C(2)	149.6 (1)	149.5 (1)
C(5)—C(1)—C(6)	110.6 (1)	110.4 (1)	C(3)—C(5)—C(2)	137.4 (2)	136.2 (1)
C(5)—C(1)—C(2)	58.66 (9)	58.6 (1)	C(4)—C(5)—C(1)	133.3 (1)	134.8 (1)
C(6)—C(1)—C(2)	119.7 (1)	119.8 (1)	C(3)—C(5)—C(1)	120.3 (1)	120.7 (1)
C(5)—C(2)—C(1)	58.76 (9)	58.7 (1)	C(2)—C(5)—C(1)	62.6 (1)	62.7 (1)
C(5)—C(3)—C(7)	116.3 (1)	115.2 (1)	O(2)—C(6)—C(1)	110.9 (1)	110.7 (1)
C(5)—C(3)—C(4)	57.9 (1)	58.31 (9)	O(1)—C(7)—O(2)	118.2 (1)	118.3 (1)
C(7)—C(3)—C(4)	119.3 (1)	118.1 (1)	O(1)—C(7)—C(3)	124.1 (1)	123.6 (1)
C(5)—C(4)—C(3)	58.4 (1)	58.35 (9)	O(2)—C(7)—C(3)	117.7 (1)	118.2 (1)
C(4)—C(5)—C(3)	63.7 (1)	63.3 (1)			

of other crystals identical to that described above, as well as a tiny plate (0.16 × 0.12 × 0.04 mm) that gave a diffraction pattern corresponding only to the cell A. The results of that particular experiment have been reported briefly by de Meijere *et al.* (2002).

3. Results and discussion

The coexistence of two sublattices implies that crystal (1) has a composite nature. Indeed, composite or intergrowth crystal structures are defined as those 'where basic structure consists of two or more subsystems each with its own space-group symmetry (neglecting mutual interaction) such that, in general, the corresponding lattices are incommensurate. This means that these lattices are not sublattices of a common one. These crystals . . . show more than one set of main reflections.' (*International Tables for Crystallography*, 1992, Vol. C, pp. 797.) According to this definition, one can regard crystal (1) as a composite but commensurate one, because the lattices A and B are the sublattices of the common orthorhombic one and can be indexed by three-dimensional indices.

Usually in the case of composite structures, these sublattices belong to the same crystal system and the crystal is described in terms of the (3 + *n*)-dimensional space-group formalism developed for incommensurate structures (see, for example, Janner, 1995; Coppens, 1995). However, the simple approach used in this paper (separate refinement of the two sublattices using the subsets of the reflections) is not entirely new, and recently it was successfully applied for the refinement of the structures of rare-earth boride carbides (Oeckler *et al.*, 2002).

Composite crystals are typical for compounds that include several chemical components, often with complex stoichiometry; different chemical components form the separate sublattices. In the case of lactone (1), we have a very unusual example of a composite crystal with two sublattices formed by identical molecules. In fact, there are two polymorphs in the same crystal. To the best of our knowledge, this is the first composite molecular organic crystal described. In the case of structure (1), we are not dealing with a 'classical' composite crystal, where both lattices are interpenetrating, but rather with a crystal containing crystal domains of two different types corresponding to different polymorphs (polytypes, see below). A discussion on the formation of similar crystals can be found by Oeckler *et al.* (2002), and the structure of (1) confirms the need to have a common structural element for forming intergrowth crystals of this type.

Not surprisingly, the molecular geometry of lactone (1) in structures A and B is almost identical (Fig. 2, Table 2) and corresponds well to the expected one. Boese (1992) described the deviation of the geometry of spiropentane from ideal C_{2v}-symmetry in terms of bending (φ) and twisting (ψ) angles. It was shown that bending is energetically more favourable than twisting, and in ethano-bridged spiropentane the parameters are $\varphi = 154.0°$ and $\psi = 80.0°$ (Boese, 1992). Replacement of the two-atom bridge by the three-atom one in molecule (1) results in a relaxation in the strain of the molecule and the corresponding values are $\varphi = 163.8°$ and $\psi = 87.4°$. This means that the spiropentane fragment of molecule (1) shows only slight bending and almost no twisting is observed.

In crystals of both modifications, molecules (1) form loose layers, perpendicular to the (001) direction (Fig. 3). The layers
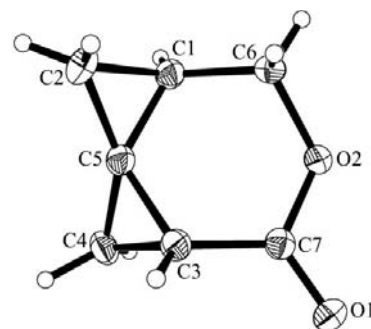

Figure 2
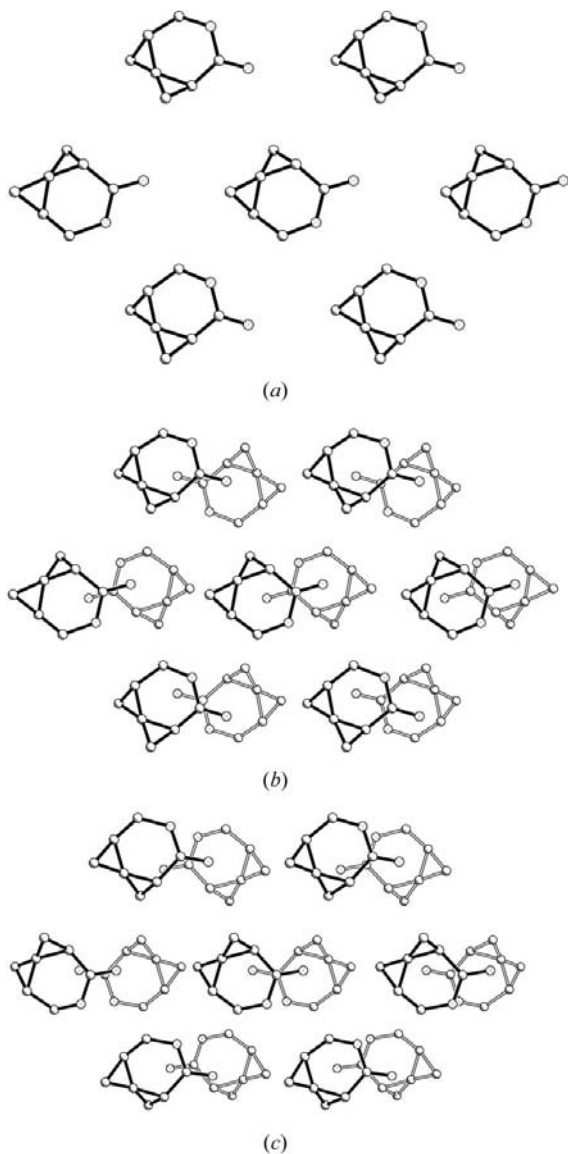Molecular structure of (1) and labelling scheme.

Figure 3
Layer of molecules (1) in crystal (*a*) and packing diagram of structures *A* (*b*) and *B* (*c*) (viewed along *c* axis, *b* axis to the right, H atoms are omitted).

Table 3
Shortest intermolecular contacts in structure *A*.

$D-\mathrm{H}\cdots A$	$d(D-\mathrm{H})$ (Å)	$d(\mathrm{H}\cdots A)$ (Å)	$d(D\cdots A)$ (Å)	$\angle(\mathrm{DHA})$ (°)
C(2)—H(2B)···O(1)^{i}†	0.97 (2)	2.67 (2)	3.632 (2)	173 (2)
C(4)—H(4B)···O(1)^{ii}†	0.98 (1)	2.44 (2)	3.404 (2)	170 (2)
C(6)—H(6B)···O(1)^{iii}	0.98 (2)	2.56 (2)	3.462 (2)	153 (1)
C(2)—H(2A)···O(1)^{iii}	1.03 (2)	2.64 (2)	3.501 (2)	141 (2)

Symmetry transformations used to generate equivalent atoms: (i) $x, y + 1, z$; (ii) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$; (iii) $-x + \frac{1}{2}, -y, z - \frac{1}{2}$. † Intra-layer contact.

Table 4
Shortest intermolecular contacts in structure *B*.

$D-\mathrm{H}\cdots A$	$d(D-\mathrm{H})$ (Å)	$d(\mathrm{H}\cdots A)$ (Å)	$d(D\cdots A)$ (Å)	$\angle(\mathrm{DHA})$ (°)
C(2)—H(2A)···O(1)^{i}†	0.98 (2)	2.75 (2)	3.698 (2)	164 (2)
C(4)—H(4A)···O(1)^{ii}†	0.89 (2)	2.55 (2)	3.427 (2)	169 (2)
C(6)—H(6B)···O(1)^{iii}	0.94 (2)	2.58 (2)	3.445 (2)	154 (2)
C(4)—H(4B)···O(1)^{iv}	0.93 (2)	2.65 (2)	3.585 (2)	177 (2)
C(1)—H(1A)···O(2)^{v}	0.97 (2)	2.68 (2)	3.546 (2)	148 (2)

Symmetry transformations used to generate equivalent atoms: (i) $x, y + 1, z$; (ii) $-x + 2, y + \frac{1}{2}, -z + \frac{1}{2}$; (iii) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (iv) $x, -y + \frac{3}{2}, z - \frac{1}{2}$; (v) $-x + 1, -y + 2, -z$. † Intra-layer contact.

in Tables 3 and 4. The parameters of the contacts correspond well to the characteristics of weak C—H···O hydrogen bonds formed by methylene groups of three-membered rings with the O atoms of carbonyl groups (Allen *et al.*, 1996).

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are almost identical in structures of the orthorhombic (*A*) and monoclinic (*B*) forms. However, in structure *A* the molecules of the next layer are connected to the molecules of the original layer by twofold axes, and in structure *B* by a *c*-glide plane. This means that structures *A* and *B* differ only by arrangement of the layers and can be regarded as polytypes. There are a number of short C—H···O contacts between molecules of both structures. The shortest ones (O···H ≤ 2.7 Å) are listed