The Photodimer 6,7-Dimethyl-*cis-anti-cis*-tricyclo[5,3,0,0²·⁶]decane-3,10-dione

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Abstract, $C_{12}H_{16}O_2$, orthorhombic, *Pccn*, $a = 10\cdot11(5)$, $b = 7\cdot53(3)$, $c = 14\cdot05(5)$ Å, $Z = 4$, $D_x = 1\cdot19$ g cm^{-3}, M.W. 192·2, $R = 9\%$. The dimer has *anti* configuration, the twofold axis being parallel to **c**. The asymmetric unit contains half the molecule.

Introduction. The present cyclobutane dimer was earlier identified as one of six products formed by ultraviolet irradiation of 3-methylcyclopent-2-enone in solution (Mark *et al.*, 1971; Reinfried, Belluš & Schaffner, 1971). Although the approximate molecular structure could be derived from infrared, n.m.r. and mass spectroscopy it turned out to be difficult to assign the correct configurations (*syn* or *anti*) to dimers III and IV by these methods alone (Fig. 1). In view of this uncertainty it was decided to carry out a crystal structure determination of the isomer which was more abundant and available in crystalline form.

A needle-shaped single crystal of dimensions $0\cdot2 \times 0\cdot2 \times 0\cdot5$mm was mounted along **c** on a four-circle diffractometer (Philips PW1100) and 1100 independent reflexions were recorded at room temperature with continuous ω–2θ scans, Mo *K*α radiation, $\lambda = 0\cdot7107$ Å, graphite monochromator. The systematic extinctions were found to be *hk*0: $h + k = 2n + 1$; 0*kl*: $l = 2n + 1$; *h*0*l*: $l = 2n + 1$. Unique space group *Pccn*. By monitoring three reflexions it was found that the crystal deteriorated during exposure to X-rays, the decrease in intensity of the reference reflexions being 20% after 24 h. At the same time, the originally transparent crystal became opaque, but did not change in morphology. All reflexions were adjusted according to the fall-off in intensity of the reference reflexions. No absorption correction was made, and standard deviations of the structure-factor amplitudes were assigned on the basis of counting statistics.

The final data were adjusted to an absolute scale by a Wilson plot and normalized structure factors were derived from the *K* curve ($K = I/\langle I \rangle$). The cumulative distribution function followed very closely the centric case, indicating that statistical methods were likely to solve this crystal structure. The computer program *LSAM* (Main, Woolfson & Germain, 1972) was used and the solution with the highest figures of merit yielded the correct structure model.

The atomic positions and anisotropic thermal parameters of the carbon and oxygen atoms were refined by the full-matrix least-squares method, the function minimized being $\sum\omega(\Delta F^2)$ where $\omega = 1/\sigma^2(F_o)$ (Busing *et al.*, 1971*b*). The final $R = \sum|\Delta F|/\sum|F_o|$ is 9% for 400 reflexions with $I > 3\sigma$.

A final difference map did not reveal the hydrogen atoms because of the high $\sigma|F_o|$ due to decomposition of the crystal. Estimated standard deviations of the parameters were calculated from the inverse of the normal equation matrix of the last least-squares cycle.
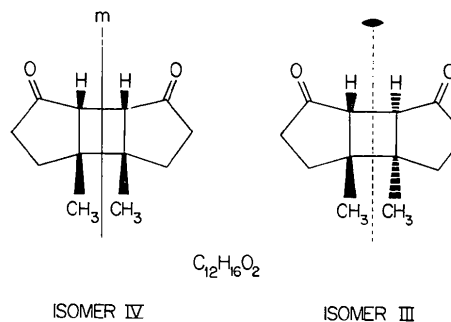

Fig. 1. Isomer IV (*syn* configuration) and isomer III (*anti* configuration) of $C_{12}H_{16}O_2$.

Table 1. *Atomic and thermal parameters*

Thermal parameters are of the form $\exp[-\{b_{11}h^2 + b_{22}k^2 + b_{33}l^3 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl\}]$. The standard deviations are in parentheses. No atomic coordinates for H atoms are given. Values are $\times 10^3$.

	x/a	y/b	z/c	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(1)	244 (1)	−4 (1)	205 (1)	11 (1)	17 (1)	8 (1)	2 (1)	−2 (1)	7 (1)
C(2)	201 (1)	173 (1)	153 (1)	10 (1)	8 (1)	4 (1)	1 (1)	0 (1)	0 (1)
C(3)	58 (1)	207 (1)	181 (1)	5 (1)	27 (3)	5 (1)	2 (1)	0 (1)	1 (1)
C(4)	512 (1)	212 (1)	91 (1)	9 (1)	33 (2)	5 (1)	3 (1)	2 (1)	0 (1)
C(5)	65 (1)	219 (1)	9 (1)	12 (1)	17 (2)	6 (1)	−5 (1)	−4 (1)	1 (1)
C(6)	205 (1)	167 (1)	42 (1)	9 (1)	14 (2)	2 (1)	−3 (1)	0 (1)	1 (1)
O	473 (1)	202 (1)	429 (1)	19 (1)	43 (2)	6 (1)	6 (1)	7 (1)	2 (1)

(a)

(b)
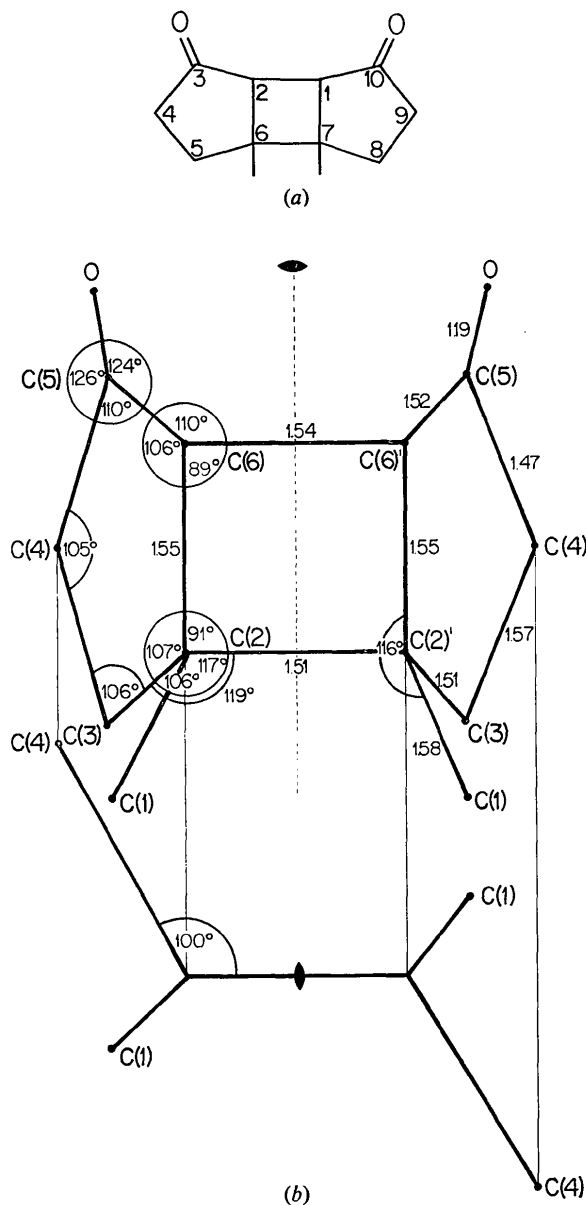
Fig. 2. (a) The numbering system for a molecule of $C_{12}H_{16}O_2$. (b) Interatomic distances (Å) and angles (°) for $C_{12}H_{16}O_2$, isomer III.

All shifts of parameters during this cycle were less than 0·1 of the e.s.d.'s. The atomic and thermal parameters with the e.s.d.'s are shown in Table 1. A list of structure factors is available.*

Discussion. Figs. 2 and 3 show the crystal and molecular structure, the numbering system used, and the bond lengths and angles. The standard deviations of the bond lengths range from 0·005 to 0·01 Å, and from 0·5 to 1·0° for the angles (Busing et al., 1971a).

The molecule consists of two monomers, joined at C(2) and C(6), and related by a twofold axis. The fusion was expected to produce significant strains in the four- and five-membered rings. However, a least-squares fit of planes through atoms C(1), C(2), C(3), C(4), C(5) and through atoms C(6), C(6)', C(2), C(2)' revealed only small deviations from planarity, the maximum values being 0·16 Å for atom C(4) in the five-membered ring, and 0·03 Å for atoms C(2) and C(2)' in the four-membered ring. The two monomers are arranged in anti configuration, the inclination angle being ~100° (Fig. 2).

The C–C bond distances range from 1·47 to 1·58 Å; the value for the carbonyl bond is 1·19 Å. The existence of the short bond (1·47 Å) between C(5) and C(4) has been confirmed by refining X-ray data taken on a second crystal. No atomic coordinates for hydrogen atoms can be given and consequently the cis configuration of the C(6) hydrogen atom and the methyl group cannot be claimed to be established on the basis of the present analysis. The main result of this work is therefore the unequivocal assignment of the correct conformation to dimer III.
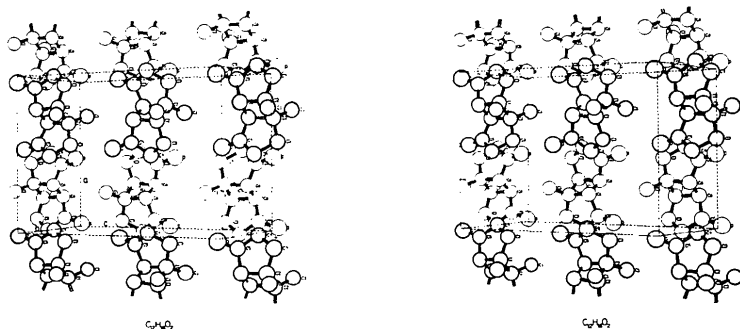
Fig. 3. Stereoscopic pair of the crystal structure of $C_{12}H_{16}O_2$ (Johnson, 1965).

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Low-Temperature Rubidium Sulphate

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Abstract. β-Rb_2SO_4, orthorhombic, *Pnam*, $a = 7.8128$ (5), $b = 10.4255$ (7), $c = 5.9694$ (5) Å (25°C); $Z = 4$, calculated density 3.647 g cm^{-3}. Crystals were grown from a melt of Rb_2SO_4. The structure has been refined by least-squares methods to give an R value of 0.055 for 634 diffractometer-measured reflexions. The present work has confirmed the general features of the atomic arrangement reported by Ogg [*Phil. Mag.* (1928). **5**, 354–367]. The rubidium ions are surrounded by nine or eleven oxygen atoms. The SO_4^{2-} tetrahedra are regular with an average S–O distance of 1.474 Å.

Introduction. This work was undertaken as part of a study to provide additional information about the dimensions of the sulphate ion. The structure of β-Rb_2SO_4 was originally determined without any refinement (Ogg, 1928).

Crystals were grown from a melt of Rb_2SO_4 in *pro analysi* quality from Merck, Darmstadt. The unit-cell dimensions were refined from 32 distinct reflexions measured on a Guinier powder photograph (25°C) with KCl as internal standard.

A single-crystal fragment, roughly approximating a prismatic needle grown in the [111] direction and with the dimensions $0.02 \times 0.02 \times 0.12$ mm, was used for the collection of single-crystal data. The intensities were obtained with an automatic Siemens AED diffractometer (graphite monochromator, θ–2θ scan) using Mo $K\alpha$ radiation, $\lambda = 0.7107$ Å. From a total of about 1000 independent reflexions measured up to $\theta = 35°$, 634 were considered to be observed with $\sigma(I)/I < 0.5$. The net intensities were corrected for Lorentz, polarization and absorption ($\mu = 214$ cm^{-1}) effects.

The systematic absences are: $h0l$, $h \neq 2n$, and $0kl$, $k + l \neq 2n$, which is characteristic of the space group $Pna2_1$ and its centrosymmetric equivalent $Pnam$. Since all statistical tests applied, *e.g.* the $N(z)$ test of Howells, Phillips & Rogers (1950), indicated a centric distribution, a centre of symmetry was assumed, *i.e.* space group $Pnam$ (see below).

The structure was redetermined using Patterson and Fourier methods giving atom positions close to those reported by Ogg (1928). A few least-squares cycles, with anisotropic thermal parameters for all atoms,

Table 1. *Atomic coordinates and temperature factors*

Standard deviations are given in parentheses. The anisotropic temperature factors are of the form
$\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$. The B_{ij} values below are multiplied by 10^4.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Rb(1)	0.6750 (2)	0.4097 (1)	$\frac{1}{4}$*	67 (2)	32 (1)	95 (1)	0 (2)	0*	0*
Rb(2)	−0.0116 (2)	0.7030 (1)	$\frac{1}{4}$*	59 (2)	37 (1)	134 (3)	6 (2)	0*	0*
S	0.2380 (3)	0.4191 (3)	$\frac{1}{4}$*	38 (4)	21 (3)	58 (5)	−4 (5)	0*	0*
O(1)	0.0471 (11)	0.4137 (10)	$\frac{1}{4}$*	44 (13)	53 (10)	196 (26)	−5 (17)	0*	0*
O(2)	0.2974 (12)	0.5532 (9)	$\frac{1}{4}$*	92 (15)	38 (10)	137 (23)	−61 (18)	0*	0*
O(3)	0.3030 (8)	0.3540 (7)	0.0497 (9)	100 (10)	37 (6)	111 (14)	−1 (12)	62 (21)	−50 (18)

* Parameter fixed by symmetry.