Fig. 1. Molecular structure of (2) with crystallographic numbering scheme.

GOF = 2·0638, $(\Delta/\sigma)_{max} = 0·02$. Highest peak in final difference Fourier map = 0·34 e Å^{-3}. Atomic scattering factors of C, N, O, Si and H atoms and f' and f'' values taken from *International Tables for X-ray Crystallography* (1974).*

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* Lists of structure factors, r.m.s. amplitudes, anisotropic thermal parameters, H-atom coordinates, and phenyl-ring intramolecular bond distances and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39915 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. The final atomic parameters are listed in Table 1. Representative bond distances, angles, and torsional angles are listed in Table 2.

The molecular structure of the title compound is shown in Fig. 1 along with the crystallographic numbering scheme. Thus the structure of the compound is unambiguously shown to be isomer (2). All bond lengths and bond angles are fully consistent with literature values. The shortest intermolecular contact was 3·416 (2) Å between O(1) and C(2). There were no others shorter than 3·5 Å.

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erythro-2-Methoxymethyl-2,4-dimethylglutaric Anhydride,* $C_9H_{14}O_4$

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Abstract. $M_r = 186·2$, monoclinic, $P2_1/c$, $a = 6·554$ (1), $b = 7·297$ (3), $c = 20·983$ (4) Å, $\beta = 95·69$ (2)°, $V = 998·6$ (5) Å^3, $Z = 4$, $D_x = 1·238$ (6), $D_m = 1·229$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0·70926$ Å, $\mu = 0·10$ mm^{-1}, $F(000) = 400$, m.p. 334 K, final $R = 0·064$ for 2227 unique reflexions measured at room temperature. The oxacyclohexane ring has a half-boat conformation with C(4) at the tip. The dihedral angle between the planes of the sp^2 bonds of C(2) and C(6) is 7·9 (5)°. The average distances in the 1-oxacyclohexane-2,6-dione fragment are C=O 1·19 (2), C—O 1·38 (3), $C(sp^2)$—$C(sp^3)$ 1·49 (3), $C(sp^3)$—$C(sp^3)$ 1·51 (3) Å.

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* *erythro*-3-Methoxymethyl-3,5-dimethyl-1-oxacyclohexane-2,6-dione.

Introduction. The preparation of pure *threo* and *erythro* isomers of 2-methoxymethyl-2,4-dimethylglutaric acids, their anhydrides and dimethyl esters is important for the study of stereoregular polymethacrylic acids and polymethacrylates and for the preparation of their pure oligomers. The preparation of pure stereoisomers and the identification of *erythro* isomers of anhydrides was described by Ševčik, Doskočilová & Prádný (1981). The structure of the title compound was required for the interpretation of spectra and for the study of optical properties of related compounds. The molecular structure of the anhydride enables one to determine the configuration of the derived compounds prepared under the supervision of NMR. Optical measurements indicated the possibility of separation of enantiomeric forms by crystallization (Ševčik *et al.*, 1981) but only crystals showing systematic extinctions corresponding to space group $P2_1/c$ were suitable for single-crystal X-ray measurements.

Experimental. Crystals were grown from an acetone–cyclohexane mixture (1:1) as transparent regular sticks. D_m measured pycnometrically in *n*-heptane. Space-group determination based on Weissenberg photographs. Syntex $P2_1$ diffractometer (extinction checked by ψ scan). Unit-cell parameters refined from 18 reflexions with $11° < 2\theta < 26°$ using spherical samples mounted on glass fibers; differences among the parameters determined for five different samples were less than 1·5 e.s.d.'s. Spherical crystal, $\varnothing = 0.8$ mm, fixed in a capillary (crystals rapidly sublimed). $\theta/2\theta$ scan. 2922 reflexions measured up to $\sin\theta/\lambda = 0.705$ Å^{-1}; 695 classified as unobserved with $I < 1.96\sigma_I$, where σ_I was taken from counting statistics. Max. diffraction indices 9, 10, 29. Other measurement details as in Hašek, Hlavatá & Huml (1977). Long-term stability of three standard reflexions better than 1·2%. No corrections for absorption or extinction. Intensity statistics gave $\langle |E| \rangle = 0.789$, $\langle |E|^2 - 1 \rangle = 0.994$. Structure determined with *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined by block-diagonal least-squares procedure. $\sum w|F_o - F_c|^2$ minimized; $w = [\sigma^2 + (0.015F)^2]^{-1}$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974), those for H being taken as a spherical approximation of the bonded atom in the hydrogen molecule. The refinement (all non-H atoms with anisotropic and H atoms with isotropic temperature factors) gave $R = 0.064$, $wR = 0.082$, $S = 1.07$ for 2227 observed reflexions and 174 parameters. For all 2509 measured reflexions $R = 0.068$, $wR = 0.082$, $S = 1.01$. $\Delta/\sigma < 0.3$ for all refined parameters. Highest peak in final difference map 0.24 e Å^{-3}. Structure refinement and calculation of geometry performed with modified *NRC* (Ahmed, Hall, Pippy & Huber, 1966) and *IMC* (Hašek, 1981) programs.

Discussion. The final coordinates of the non-H atoms with B_{eq} values (Hamilton, 1959) and those of the H atoms with B_{iso} are in Tables 1 and 2. The numbering scheme, bond distances and selected interbond angles are shown in Fig. 1. Interbond angles not given in Fig. 1 and Newman projections have been deposited.* Table 3 lists selected torsion angles.

The oxacyclohexane ring has an approximate half-boat conformation [spherical puckering coordinates (Cremer & Pople, 1975): $Q = 0.42$ Å, $\theta = 52.9°$, $\varphi = 197.1°$]. The conformation is influenced mainly by the two nearly parallel planes of the sp^2 orbitals of C(2) and C(6) with a dihedral angle of 7·9 (5)° (Table 4, planes a,b). The weighted mean plane through C(3), C(2), O(1), C(6) [$\chi^2 = 129$, max. deviation 0·014 (2) Å] fits the condition of planarity better than that through C(2), O(1), C(6), C(5) [$\chi^2 = 617$, max. deviation = 0·034 (2) Å]. Atoms O(1), C(2), C(3), C(5), C(6) lie only approximately in a plane [$\chi^2 = 3578$, max. deviation = 0·068 (2) Å]. This mean plane forms a dihedral angle of 43·6° with the plane of the three C(sp^3) atoms in the ring (Table 4).

Using the Cambridge Database (Allen *et al.*, 1979), the 1-oxacyclohexane-2,6-dione fragment was only found in four structures: bromovalerone anhydride (Hoehne, 1966) ($P2_12_12_1$, $R = 0.17$); β-chloroglutaric anhydride (Koer, de Kok & Romers, 1972) ($C2/c$, $R = 0.12$); 3-phenyl-1-oxacyclohexane-2,6-dione (Bocelli & Grenier-Loustalot, 1982) ($P2_1/n$, $R = 0.09$); 1-oxacyclohexane-4-spirocyclopentane-2,6-dione (Bocelli, Grenier-Loustalot & Urbanczyk-Lipkowska, 1982) ($P2_12_12_1$, $R = 0.07$) (Table 5). As β-chloroglutaric anhydride contains two symmetrically independent molecules, six independent fragments can be discussed. In spite of the fact that only the title compound and 1-oxacyclohexane-4-spirocyclo-pentane-2,6-dione have e.s.d.'s for distances under 0·01 Å, the average geometry fits the expectation well. The average distances in the fragment are C=O 1·19 (2), C–O 1·38 (3), C(sp^2)–C(sp^3) 1·49 (3), C(sp^3)–C(sp^3) 1·51 (3) Å. Interbond angles around the carbonyls are C–C=O 116 (1), O–C–C 118 (3), O=C–C 126 (2)° and angles C(sp^2)–C(sp^3)–C(sp^3) 112 (2), C(sp^3)–C(sp^3)–C(sp^3) 109 (4)°. Large differences among torsion angles of the fragment (Table 5) show the strong influence of different substituents on the conformation of the ring. The mean torsion angles of the 1-oxacyclohexane-2,6-dione are C–C–O–C 6 (2), O–C–C–C 27 (11), C(sp^2)–C(sp^3)–C(sp^3)–C(sp^3) 53 (7)°. The angles between the mean planes O(1), C(2), C(6) and C(2), C(3), C(5), C(6) are in all

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* Lists of structure factors, anisotropic thermal parameters, additional angles and Newman projections have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39928 (39 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

cases less than 6°. The angles between the mean planes C(2), C(3), C(5), C(6), and C(3), C(4), C(5) are in the interval 44–52°.

Table 1. *Final positional parameters* ($\times 10^4$) *with e.s.d.'s in parentheses and* B_{eq} *values* (Å^2) *of the non-*H *atoms*

$$B_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j.$$

	x	y	z	B_{eq}
O(1)	5847 (2)	3023 (2)	6564 (1)	4·15
C(2)	5154 (3)	1615 (3)	6171 (1)	4·12
C(3)	2873 (2)	1224 (2)	6056 (1)	3·65
C(4)	1703 (2)	2164 (2)	6556 (1)	3·85
C(5)	2364 (2)	4121 (2)	6700 (1)	3·73
C(6)	4618 (3)	4225 (3)	6861 (1)	4·43
O(7)	5509 (3)	5291 (3)	7213 (1)	9·12
O(8)	6435 (2)	792 (3)	5928 (1)	7·18
C(9)	1268 (3)	4978 (4)	7233 (1)	6·71
C(10)	2546 (4)	−856 (3)	6093 (1)	6·23
C(11)	2180 (3)	1837 (3)	5377 (1)	4·35
O(12)	2751 (2)	3679 (2)	5289 (1)	4·84
C(13)	2402 (4)	4251 (4)	4643 (1)	6·25

Table 2. *Final positional parameters* ($\times 10^3$) *and* B_{iso} *values* (Å^2) *of the* H *atoms and their e.s.d.'s*

	x	y	z	B_{iso}
H(41)	186 (3)	151 (3)	695 (1)	4·7 (4)
H(42)	38 (3)	221 (3)	640 (1)	5·1 (4)
H(51)	215 (3)	480 (2)	633 (1)	3·7 (4)
H(91)	1 (4)	496 (4)	714 (1)	10·0 (9)
H(92)	174 (4)	624 (4)	733 (1)	6·9 (6)
H(93)	141 (5)	406 (4)	764 (1)	9·7 (8)
H(101)	330 (4)	−145 (4)	577 (1)	8·1 (7)
H(102)	314 (4)	−130 (3)	650 (1)	7·5 (6)
H(103)	108 (3)	−107 (3)	602 (1)	6·0 (5)
H(111)	70 (3)	167 (3)	528 (1)	4·1 (4)
H(112)	282 (3)	104 (3)	507 (1)	4·7 (4)
H(131)	312 (4)	354 (4)	438 (1)	8·7 (7)
H(132)	93 (4)	421 (4)	449 (1)	8·9 (7)
H(133)	277 (4)	531 (4)	460 (1)	9·1 (8)

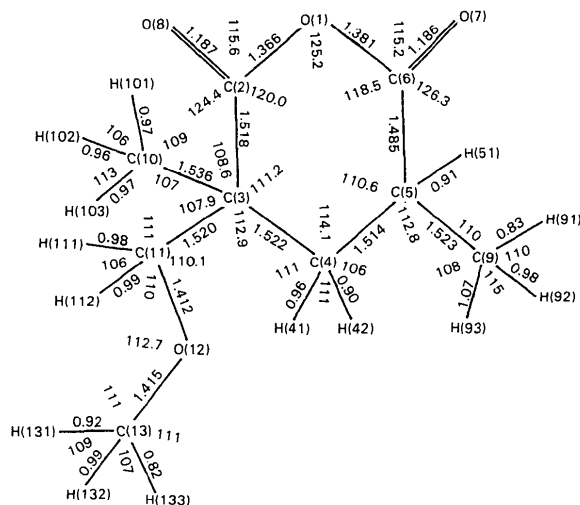

Fig. 1. The numbering scheme, interatomic distances (Å) and bond angles (°). E.s.d.'s of the distances are 0·002 Å (or 0·03 Å for bonds including H atoms). E.s.d.'s of the interbond angles are 0·1–0·2° (or 1–3° for angles including H atoms). [Angle C(6)–C(5)–C(9) is 110·1°.]

Table 3. *Selected torsion angles* (°) *(e.s.d.'s* $<0\cdot3°$)

C(4)–C(5)–C(6)–O(7)	−149·1
C(4)–C(3)–C(2)–O(8)	165·5
C(3)–C(4)–C(5)–C(9)	−176·1
C(5)–C(4)–C(3)–C(10)	163·5
O(1)–C(2)–C(3)–C(11)	−136·3
C(5)–C(4)–C(3)–C(11)	−76·4
C(4)–C(3)–C(11)–O(12)	68·6
C(3)–C(11)–O(12)–C(13)	171·8

Table 4. *Weighted mean planes with deviations of selected atoms* ($\text{Å} \times 10^3$) *and dihedral angles* (°)

E.s.d.'s of angles are $<0\cdot5°$, those of deviations $<0\cdot005$ Å. The asterisks denote atoms excluded from the plane definition.

Plane	Deviations from the mean plane							χ^2
a	O(1)	C(2)	C(3)	O(8)	C(6)*	O(7)*	C(9)*	26·8
	1(1)	−8(2)	2(2)	3(2)	75(2)	−8(2)	−175(3)	
b	O(1)	C(2)	C(6)	O(7)	C(2)*	C(3)*	O(8)*	46·1
	2(1)	−12(2)	3(2)	5(2)	−95(2)	294(2)	13(2)	
c	C(3)	C(4)	C(5)	C(2)*	C(6)*	C(9)*	C(10)*	0·0
	—	—	—	−979(2)	−1101(2)	−96(3)	−411(3)	
d	C(9)	C(5)	C(4)	C(3)	C(10)			6997
	−63(2)	−54(2)	122(2)	41(2)	−181(3)			
e	O(1)	C(3)	C(5)	C(6)	O(7)	O(8)		12234
	−4(1)	−12(2)	−98(2)	107(2)	−14(2)	−83(2)	79(2)	
f	C(10)	C(11)	O(12)	C(13)	C(3)*	C(6)*	O(7)*	13510
	99(3)	−113(2)	1(1)	99(2)	−10(2)	86(2)	247(2)	
g	H(41)	C(4)	C(3)	C(11)	H(112)			237
	267(20)	−1(2)	−2(2)	0(2)	150(20)			

Selected angles between planes: *a–b* 7·9, *a–c* 39·9, *b–c* 47·8, *d–e* 52·6, *d–f* 126·4, *e–f* 84·7, *d–g* 67·6°.

Table 5. *Torsion angles* (°) *of the* 1-*oxacyclohexane-2,6-dione fragment for six molecules*

E.s.d.'s are $<1°$ for compounds (3), (4) and (5), and less than 3° for (1) and (2).

Compound*	(1)	(2)	(2b)	(3)	(4)	(5)
C(5)–C(6)–O(1)–C(2)	6·6	4·7	3·3	−9·1	−3·3	−6·3
C(6)–O(1)–C(2)–C(3)	7·7	−8·2	−5·2	−7·7	4·0	−2·8
C(4)–C(5)–C(6)–O(1)	15·6	27·6	25·6	43·2	31·3	33·2
C(1)–C(2)–C(3)–C(4)	−45·9	−21·6	−22·4	−10·5	−35·5	−16·1
C(3)–C(4)–C(5)–C(6)	−48·5	−55·0	−50·9	−60·4	−55·9	−52·4
C(2)–C(3)–C(4)–C(5)	66·2	51·8	49·2	44·9	59·5	43·8

* (1) Bromovalerone anhydride. (2) β-Chloroglutaric anhydride. (3) 3-Phenyl-1-oxacyclohexane-2,6-dione. (4) 1-Oxacyclohexane-4-spirocyclopentane-2,6-dione. (5) Title compound.

The 1·2 Hz splitting observed in the NMR spectrum of the title compound (Ševčík *et al.*, 1981) for bands of the proton H(112) (δ 3·65, 3·75) and for bands of proton H(41) (δ 1·51, 1·65, 1·78) is unambiguously interpreted as resulting from coupling of these protons over the four bonds H(41)–C(4)–C(3)–C(11)–H(112) forming a 'W' shape and lying approximately in one plane [$\chi^2 = 237$, max. deviation 0·27 (2) Å] (Table 4, plane *g*).

The geometry of the whole non-H skeleton of the molecule may be described by the three mean planes *d,e,f* in Table 4. The max. deviation of atoms included in the plane definition from these mean planes is only 0·181 (3) Å for C(10). The common plane of the
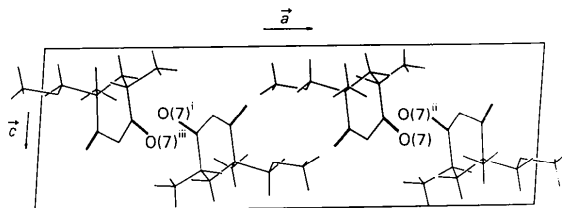
Fig. 2. Projection of the unit cell along the *b* axis.

carbonyls is roughly perpendicular to that of the methoxymethyl chain. The plane of the three $C(sp^3)$ atoms in the ring and two methyl substituents forms angles of 52·6 (5), 126·4 (5)° with the carbonyl and methoxymethyl mean planes, respectively. O(12) is thus in a favorable position with respect to H(51) of the same molecule: angle O(12)—H(51)—C(5) 123·6 (13°, distance O(12)—H(51) 2·41 (2) Å.

Crystal packing shown in projection along the *b* axis in Fig. 2 is mainly determined by van der Waals interactions. No intermolecular distances shorter than the sum of van der Waals radii were observed.

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Structure of 2,2-Dimethyl-1,3-dioxane-4,5,6-trione 5-(2,4-Dinitrophenylhydrazone), C₁₂H₁₀N₄O₈

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Abstract. $M_r = 241·25$, monoclinic, $P2_1/c$, $a = 14·236$ (12), $b = 5·220$ (5), $c = 20·111$ (15) Å, $\beta = 99·4$ (1)°, $V = 1474·4$ Å³, $Z = 4$, $D_x = 1·32$, $D_m = 1·35$ (1) g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0·7107$ Å, $\mu = 1·00$ cm⁻¹, $F(000) = 460$, room temperature, final $R = 0·072$ for 1089 independent observed reflections. In the structure the amine hydrogen atom H(7) forms a bifurcated intramolecular hydrogen bond to the *ortho*-nitro group and to a carbonyl oxygen atom. The two H(7)···O distances are equivalent within experimental error. The N(8)—C(9)—C(10) angle is larger than the N(8)—C(9)—C(20) angle by almost 15° so that this bond can be accommodated. The dioxane ring is in the envelope conformation.

Introduction. Our studies of the structural chemistry of phenylhydrazones have shown that the amine hydrogen atom H(7) has a strong proclivity to intramolecular

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† Deceased.