O(4)	0.4061 (7)	0.6544 (6)	0.4638 (5)	0.073 (2)
C(1)	0.6712 (11)	0.5381 (9)	0.2628 (8)	0.066 (4)
C(2)	0.8148 (11)	0.6577 (10)	0.3849 (9)	0.062 (4)
C(3)	0.9219 (11)	0.7466 (10)	0.4847 (10)	0.066 (4)
C(4)	1.0608 (10)	0.8626 (10)	0.6133 (10)	0.090 (5)
C(5)	0.2039 (15)	0.3711 (12)	0.1679 (12)	0.133 (7)
C(6)	0.0892 (16)	0.2810 (13)	0.0353 (12)	0.150 (7)
C(7)	0.3750 (14)	0.8789 (12)	0.2718 (12)	0.111 (6)
C(8)	0.4043 (14)	0.9587 (11)	0.1714 (12)	0.112 (6)

Table 2. *Selected geometric parameters (Å, °)*

P(1)—O(1)	1.557 (6)	P(1)—O(2)	1.571 (5)
P(1)—O(4)	1.460 (5)	P(1)—C(1)	1.813 (9)
O(1)—C(7)	1.447 (13)	O(2)—C(5)	1.435 (13)
O(3)—C(1)	1.420 (10)	C(1)—C(2)	1.479 (9)
C(2)—C(3)	1.138 (10)	C(3)—C(4)	1.473 (10)
C(5)—C(6)	1.336 (14)	C(7)—C(8)	1.385 (18)
O(1)—P(1)—O(2)	103.2 (3)	O(1)—P(1)—O(4)	116.9 (3)
O(2)—P(1)—O(4)	114.2 (3)	O(1)—P(1)—C(1)	101.2 (4)
O(2)—P(1)—C(1)	105.5 (3)	O(4)—P(1)—C(1)	114.1 (4)
P(1)—O(1)—C(7)	121.1 (6)	P(1)—O(2)—C(5)	121.7 (6)
P(1)—C(1)—O(3)	110.0 (5)	P(1)—C(1)—C(2)	110.3 (5)
O(3)—C(1)—C(2)	114.8 (7)	C(1)—C(2)—C(3)	176.2 (10)
C(2)—C(3)—C(4)	179.5 (10)	O(2)—C(5)—C(6)	114.8 (1)
O(1)—C(7)—C(8)	112.2 (9)		
O(2)—P(1)—O(1)—C(7)	69.3 (6)	O(4)—P(1)—O(1)—C(7)	−56.9 (6)
C(1)—P(1)—O(1)—C(7)	178.4 (5)	O(1)—P(1)—O(2)—C(5)	−154.2 (7)
O(4)—P(1)—O(2)—C(5)	−26.2 (8)	C(1)—P(1)—O(2)—C(5)	99.9 (7)
O(1)—P(1)—C(1)—O(3)	−166.5 (4)	O(2)—P(1)—C(1)—O(3)	−59.2 (5)
O(1)—P(1)—C(1)—C(2)	65.9 (7)	O(2)—P(1)—C(1)—C(2)	173.2 (6)
O(4)—P(1)—C(1)—O(3)	67.0 (5)	P(1)—O(1)—C(7)—C(8)	−154.7 (5)
O(4)—P(1)—C(1)—C(2)	−60.6 (7)	P(1)—C(1)—C(2)—C(3)	79.6 (15)
P(1)—O(2)—C(5)—C(6)	175.3 (8)	C(1)—C(2)—C(3)—C(4)	−161 (10)
O(3)—C(1)—C(2)—C(3)	−45.3 (15)		

SHELXTL-Plus (Sheldrick, 1990) was used for data collection, structure solution by direct methods, structure refinement and the molecular drawings.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SZ1035). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C52, 669–672

(2*R*,3*R*,5*S*,6*S*)-2,3-Diethoxy-5,6-bis(hydroxymethyl)-2,3-dimethyl-1,4-dioxane

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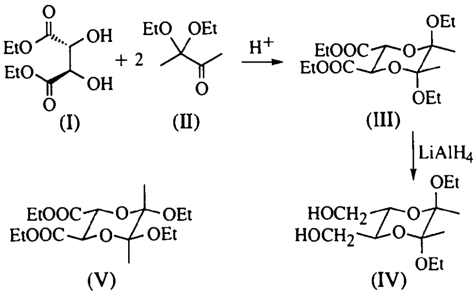
Abstract

The title compound, $C_{12}H_{24}O_6$, was synthesized and subjected to an X-ray structure determination. The aim of this structure analysis was to determine the relative orientation of two vicinal ethoxy groups in its precursor, diethyl (2*R*,3*R*,5*R*,6*R*)-5,6-diethoxy-5,6-dimethyl-1,4-dioxane-2,3-dicarboxylate, from which the title compound can be generated by a reaction that retains the absolute configuration of the molecular skeleton.

Comment

Transacetalization of diethyl tartrate, (I), with 3,3-diethoxybutan-2-one, (II), resulted diethyl (2*R*,3*R*,5*R*,6*R*)-5,6-diethoxy-5,6-dimethyl-1,4-dioxane-2,3-dicarboxylate, (III) (Berens, 1993). A structural alternative to (III) is its isomer (V). Taking into account the possible role of the anomeric effect, (V) may be somewhat higher in energy than the isomer with both ethoxy groups in axial positions (Ley, Woods & Zanotti-Gerosa, 1992; Ley, Priepke & Warriner, 1994). According to quantum-chemical calculations by the semiempirical AM1 (Dewar, Zoebisch, Healy & Stewart, 1985) and the PM3 methods (Stewart, 1989*a*,*b*), (III) is indeed energetically more favourable than (V). However, the energy differences are small [$H_f(5) - H_f(3)$: AM1 3.8 kcal mol^{-1}, PM3 2.1 kcal mol^{-1}] and probably comparable to those between different conformers of each diastereomer. Therefore, our computational results do not allow the exclusion of one of the diastereomers from our considerations. Moreover, it was not possible to rule out (V) by means of NMR data and all attempts to crystallize the product met with failure. Thus, we reduced (III) to obtain the title compound, (IV), in the form of colourless needles. Since the reaction linking

(III) and (IV) retains the absolute configuration of the molecular skeleton, an X-ray structure determination of (IV) implicitly yields the relative orientation of the ethoxy groups in (III). An *ORTEP* (Johnson, 1965) plot is given in Fig. 1, while Fig. 2 shows the arrangement of the molecules in their crystal lattice.



The result of our solid-state structure determination of (IV) proves the tentatively assumed 1,2-diaxial relationship of two vicinal ethoxy groups in (III) beyond any doubt. (IV) adopts a chair form; while within the resolution of standard NMR spectroscopy the molecule has C_2 symmetry in solution, there is no such crystallographic symmetry in the solid state.

The molecules are linked by hydrogen bonds [O16—H16···O18^i, O16—H16 = 0.781 (3), H16···O18^i = 2.019 (3), O16···O18^i = 2.773 (4) Å, and O16—H16···O18^i = 162.3 (3)°; symmetry code: (i) x+1, y, z] resulting in chains extending approximately parallel to the a axis. Although the O1···O18 distance [2.936 (4) Å] is close to twice the value of the isotropic van der Waals radius of oxygen (1.52 Å) (Bondi, 1964) and in spite of the fact that the O1···H18 distance [2.505 (2) Å] is only slightly smaller than the sum of the van der Waals radii for hydrogen (1.20 Å) and oxygen, the O1···H18—O18 moiety (which requires application of symmetry operation $x-1$, y, z to O1) contributes to the stabilization of the bonding between the molecules in the chain (Jeffrey & Saenger, 1991; Berstein, Etter & Leiserowitz, 1994). Other distances between neighbouring molecules close to the sum of the relevant van der Waals radii are those between C12 and C10 [3.729 (7) Å], C10 and O16 [3.576 (6) Å], H18 and C14 [3.037 (4) Å], and H18 and O8 [2.807 (3) Å].

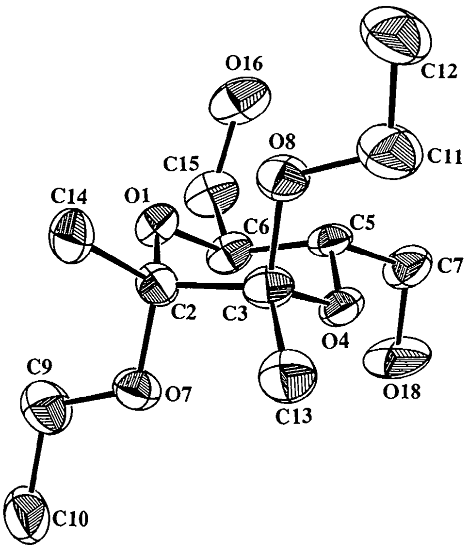


Fig. 1. Structure of (IV) in the solid state. Displacement ellipsoids are plotted at the 30% probability level.

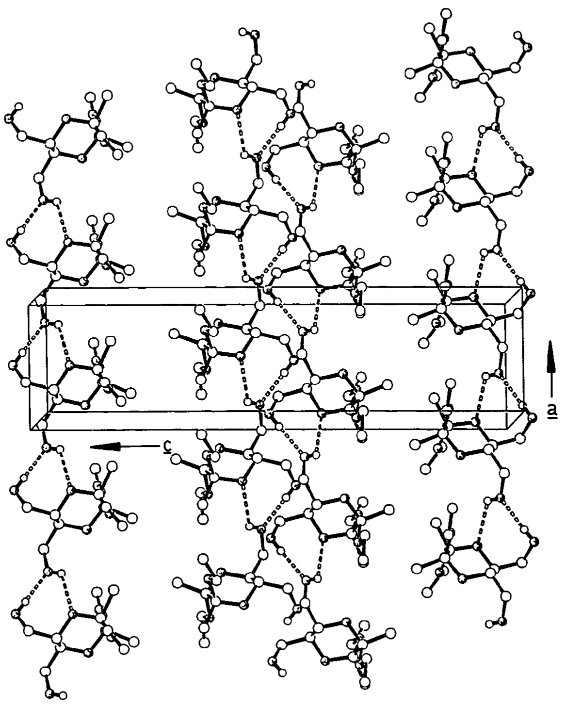


Fig. 2. Packing of the molecules in the cell (*SCHAKAL*; Keller, 1986).

Since the absolute configuration at atoms C2 and C3 was known, we did not collect a complete set of Friedel opposites. Moreover, because the differences between those Friedel opposites present in the data set turned out to be insufficient for a refinement of Flack's absolute-structure parameter (Flack, 1983; Bernardinelli & Flack, 1985), we decided to merge them.

Experimental

Transacetalization of diethyl tartrate, (I), with 3,3-diethoxybutan-2-one, (II), resulted in a 88% yield of (III) (see *Comment*). Reduction of (III) yielded the title compound, (IV), which was obtained in the form of colourless needles after recrystallization from ether/petroleum ether.

Crystal data

$C_{12}H_{24}O_6$
M_r = 264.3
Mo $K\alpha$ radiation
λ = 0.71069 Å

Orthorhombic
$P2_12_12_1$
$a = 6.078\,(1)$ Å
$b = 9.996\,(2)$ Å
$c = 23.888\,(4)$ Å
$V = 1451.3\,(4)$ Å^3
$Z = 4$
$D_x = 1.210$ Mg m^{-3}

Cell parameters from 25 reflections
$\theta = 10.2$–$19.3°$
$\mu = 0.09$ mm^{-1}
$T = 293$ K
Irregular
0.4 × 0.4 × 0.4 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3772 measured reflections
1945 independent reflections
1219 observed reflections $[I > 2\sigma(I)]$

$R_{\rm int} = 0.03$
$\theta_{\rm max} = 27.5°$
$h = -7 \rightarrow 7$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 30$
3 standard reflections frequency: 60 min intensity decay: <1%

Refinement

Refinement on F
$R = 0.054$
$wR = 0.048$
$S = 2.284$
1218 reflections
164 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\rm max} < 0.0002$
$\Delta\rho_{\rm max} = 0.3$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.3$ e Å^{-3}

Extinction correction: Zachariasen (1967), Larson (1970)
Extinction coefficient: $r^* = 6088$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O1	0.5022 (4)	0.3899 (2)	0.4196 (1)	0.0570 (9)
O4	0.2105 (4)	0.5813 (2)	0.3810 (1)	0.0569 (9)
O7	0.3023 (5)	0.3144 (3)	0.3430 (1)	0.066 (1)
O8	0.5722 (4)	0.6257 (3)	0.3559 (1)	0.067 (1)
O16	0.5205 (5)	0.4929 (4)	0.5356 (1)	0.100 (1)
O18	−0.1306 (5)	0.5478 (4)	0.4645 (1)	0.119 (2)
C2	0.4697 (6)	0.4018 (4)	0.3613 (2)	0.055 (1)
C3	0.3860 (6)	0.5424 (4)	0.3458 (1)	0.055 (1)
C5	0.2571 (5)	0.5704 (4)	0.4397 (2)	0.055 (1)
C6	0.3108 (6)	0.4266 (4)	0.4526 (2)	0.058 (1)
C7	0.0609 (7)	0.6261 (5)	0.4703 (2)	0.083 (2)
C9	0.3324 (9)	0.1754 (4)	0.3556 (2)	0.091 (2)
C10	0.1699 (8)	0.0969 (5)	0.3245 (2)	0.106 (2)
C11	0.537 (1)	0.7666 (5)	0.3458 (2)	0.106 (2)
C12	0.742 (1)	0.8377 (5)	0.3521 (2)	0.116 (3)
C13	0.2976 (8)	0.5532 (4)	0.2872 (2)	0.078 (2)
C14	0.6915 (7)	0.3684 (5)	0.3347 (2)	0.077 (2)
C15	0.3700 (8)	0.3977 (5)	0.5130 (2)	0.084 (2)

Table 2. *Selected geometric parameters (Å, °)*

O1—C2	1.413 (4)	O1—C6	1.452 (4)
O4—C3	1.413 (4)	O4—C5	1.434 (4)
O7—C2	1.410 (5)	O7—C9	1.433 (5)
O8—C3	1.425 (4)	O8—C11	1.445 (5)
O16—C15	1.426 (6)	O18—C7	1.410 (6)
C2—C14	1.527 (6)	C2—C3	1.540 (5)
C3—C13	1.503 (6)	C5—C6	1.506 (5)
C5—C7	1.506 (6)	C6—C15	1.515 (5)
C9—C10	1.464 (7)	C11—C12	1.440 (8)
C3—O4—C5	114.3 (3)	C2—O7—C9	116.3 (3)
C3—O8—C11	115.2 (3)	O7—C2—O1	110.7 (3)
O7—C2—C14	112.0 (3)	O7—C2—C3	104.7 (3)
O1—C2—C14	105.6 (3)	O1—C2—C3	111.0 (3)
C14—C2—C3	113.1 (3)	O4—C3—O8	109.8 (3)
O4—C3—C13	105.3 (3)	O4—C3—C2	111.0 (3)
O8—C3—C13	113.5 (3)	O8—C3—C2	103.3 (3)
C13—C3—C2	114.0 (3)	O4—C5—C6	108.4 (3)
O4—C5—C7	106.9 (3)	C6—C5—C7	115.1 (3)
O1—C6—C5	107.7 (3)	O1—C6—C15	106.1 (3)
C5—C6—C15	115.4 (3)	O18—C7—C5	113.6 (4)
O7—C9—C10	109.1 (4)	C12—C11—O8	109.8 (4)
O16—C15—C6	112.7 (4)	C2—O1—C6	113.7 (3)

The H atoms involved in hydrogen bonds could be located in a difference Fourier map. The remaining H atoms were placed in calculated idealized positions. The isotropic displacement parameter of each calculated H atom was fixed at 1.5 times the value of $U_{\rm eq}$ the parent atom. All H atoms were refined using the riding model. The semi-empirical calculations were performed using the *MOPAC* set of quantum-chemical routines (Stewart, 1989*c*).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *Xtal*3.2 *DIFDAT* (Hall, Flack & Stewart, 1992). Program(s) used to solve structure: *Xtal*3.2 *GENSIN* and *GENTAN*. Program(s) used to refine structure: *Xtal*3.2 *CRYLSQ*. Molecular graphics: *SCHAKAL* (Keller, 1986); *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *Xtal*3.2 *ATABLE* and *BONDLA*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1071). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 672–674

1,3-Bis(2,5-dihydro-5,5-dimethyl-2-oxo-1-pyrrolyl)-2,2-dimethyl-1,3-propanedione

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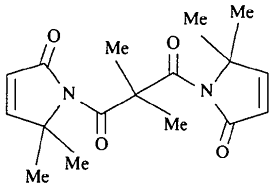
Abstract

The title compound, $C_{17}H_{22}N_2O_4$, is a linked bis-chromophore. An X-ray structure determination confirmed the restricted rotation of the alicyclic chain segment as suggested by ^{1}H NMR spectroscopic results in solution.

Comment

The photochemical behavior of 2,5-dihydro-5,5-dimethylpyrrole-2-one (Ihlefeld & Margaretha, 1992) parallels that of the pyrimidine bases in DNA, *e.g.* uracil or thymine. We have synthesized a series of 1,1′-linked bis-chromophores with different spacers. In order to characterize one of the resulting products unambiguously, an X-ray structure determination of the title compound, (I), was undertaken.



(I)

The title compound can be considered to be a derivative of 2,2-dimethylmalonic acid, where the carboxy groups are replaced by semicyclic imide systems. Both of these systems exhibit an *E* configuration (O41—C31—N51—C61—O71 and O42—C32—N52—C62—O72). In this sterically favored arrangement, the imide O atoms (O41···O71 and O42···O72) are at a maximum distance from one another. The spatial vicinity of both almost planar imide systems causes a strong steric interaction between the O71 and O72 atoms, which is reduced by a considerable distortion of the bond angle at the central C10 atom. While the C21—C10—C22 angle of 109.1 (1)° almost corresponds to that of an sp^3-hybridized C atom, the C31—C10—C32 bond angle of 123.2 (1)° is considerably enlarged.

As expected, both five-membered rings are almost flat [maximum deviation of 0.03 (2) Å in the N52—C62—C82—C92—C102 ring]. Even the least-squares planes through each of the eight-atom sets O71, N51, C61, C81, C91, C101, C31, O41 and O72, N52, C62, C82, C92, C102, C32, O42, show a maximum deviation of only −0.075 (7) Å (*PLATON*92; Spek, 1992).

The ^{1}H NMR spectrum of the title compound is remarkable as it shows two pairs of methyl proton signals for the *a priori* four equivalent methyl groups on the two heterocyclic rings. Indeed, the crystal structure suggests that the two ring carbonyl O atoms (O71 and O72) collide on rotation of the open-chain N—C(=O)—C—C(=O)—N segment and, therefore, the two pairs of methyl groups become diastereotopic.

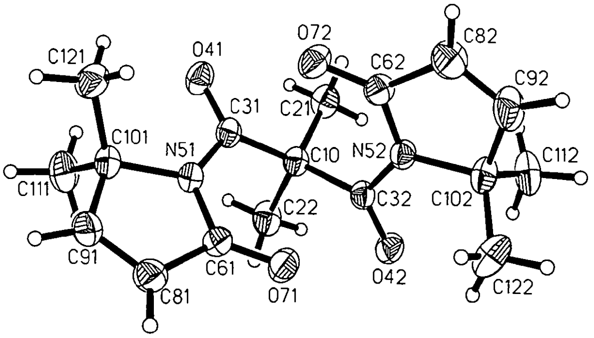


Fig. 1. *ORTEP*II drawing (Johnson, 1976), as implemented in *SHELXTL-Plus* (Sheldrick, 1992), of the title compound showing displacement ellipsoids at 30% probability and the atomic numbering scheme.

Experimental

The title compound results in 58% yield from the reaction of two moles of 2,5-dihydro-5,5-dimethylpyrrole-2-one and one mole of dimethylmalonic acid dichloride (Wrobel, 1994). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.51 (*s*, 6H), 1.55 (*s*, 6H), 1.65 (*s*, 6H), 5.86 (*d*, J = 6.1 Hz, 2H), 7.09 p.p.m. (*d*, J = 6.1 Hz, 2H). Suitable single crystals (m.p. 401–402 K) were obtained from an ethoxyethane solution.

Crystal data

$C_{17}H_{22}N_2O_4$	Cu $K\alpha$ radiation
M_r = 318.37	λ = 1.54178 Å