Data reduction: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Structure solution: *SHELXS*86 (Sheldrick, 1985). Structure refinement: *NRCVAX*. Molecular graphics: *ORTEP* (Johnson, 1965).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1106). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2(*RS*)-*r*-2-[(*RS*)-1-(4-Chlorobenzoyloxy)ethyl]-2-ethyl-1,3-dioxolan-*c*-4-ylmethyl 4-Chlorobenzoate

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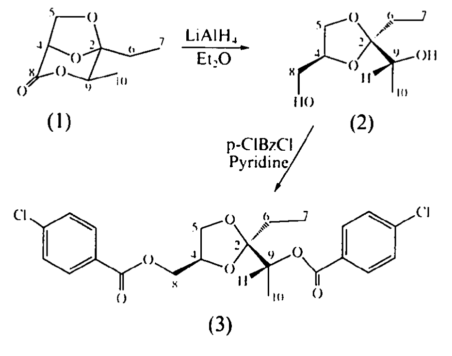
Abstract

X-ray structure analysis of the title compound, $C_{22}H_{22}Cl_2O_6$, (3), was carried out in order to determine the relative configuration at the substituent atoms C(6) and C(10) of its precursor (±)-5-ethyl-4-*endo*-methyl-3,6,8-trioxabicyclo[3.2.1]octan-2-one (1). This configuration is expected not to change during the series of reactions linking these two molecules. The solid-state structure of (3) is characterized by a contact between the bulky side chains which are both on the same side of the five-membered ring. The shortest distance between these substituents involving non-H atoms (O···C) is 3.335 (3) Å. This striking structural characteristic of the title compound is realized in at least one local minimum on the hypersurface of the free molecule since a quantum-chemical calculation employing the semi-empirical AM1 method and starting from the solid-state structure of (3) resulted in a relative minimum with a similar distance between corresponding atoms.

Comment

(±)-5-Ethyl-4-*endo*-methyl-3,6,8-trioxabicyclo[3.2.1]octan-2-one, (1), was obtained as the lower-boiling isomer from a mixture of the *endo*/*exo*-methyl diastereomers of (1) in the course of a new *β*-multistriatin synthesis. Compound (1) is similar to the multistriatins whose pheromonic activity strongly depends on the relative stereochemistry of their methyl groups. Therefore, knowledge of the relative orientation of atoms C(10) and C(6) in (1) is of interest, since it allows estimation of possible pheromonic activity of this species. ^{1}H NMR spectroscopic results obtained in solution turned out to be inconclusive in this regard. Moreover, it was not possible to obtain (1) in the form of single crystals suitable for X-ray structure determination. Thus, we prepared the title compound (3) as a crystalline derivative of (1) and determined its solid-state structure by means of X-ray crystallography.



The information regarding the relative configuration of C(10) and C(6) is retained during the reactions linking (1) and (3). Thus determination of the configuration about the C(2)—C(9) bond in (3) yields the relative orientation of the corresponding substituents in (1).

It is not difficult to see that if methyl group C(10) in (1) was in an axial position, the relative configuration at C(2) of the dioxolane system and at C(9) of its side chain in (3) would be different. Since the result of our solid-state structure determination of (3) shows that the absolute configuration at both

C(9) and C(2) in (3) is the same, we conclude that methyl group C(10) is equatorial in (1).

The sum of bond angles in the five-membered ring in (3) amounts to 532.7°, corresponding to a slightly puckered dioxolane system with a maximum deviation of the ring atoms from their best plane of 0.19 Å. At an interplanar angle of 3.5 (1)°, the phenyl substituent C(13)–C(18) and the plane defined by C(13) and its adjacent COO group are almost coplanar, while the corresponding planes defined by C(21)–C(26) and C(21)—COO enclose an angle of 9.53 (9)°. Since both the long side chains of (3) are on the same side of the dioxolane system, they approach each other relatively closely; the shortest distance between the two substituents involving at least one non-H atom occurs between O(12) and H(26) (2.552 Å). Moreover, C(26) and O(12) are only 3.335 (3) Å apart. In both cases the distances are close to the sums of the isotropic van der Waals radii (Bondi, 1964). Optimization of the structural parameters of the isolated molecule with respect to its total valence-shell energy using the semi-empirical AM1 method (Dewar, Zoebisch, Healy & Stewart, 1985) and starting from the experimentally determined molecular structure, resulted in a structure whose general shape is quite similar to that found for the molecule in the crystal lattice. Calculation of the spectrum of the normal vibrations confirmed that the optimized structure corresponds to a local minimum. Although calculated bond lengths and experimentally determined interatomic distances are not directly comparable with each other, a rough comparison is permissible. Thus, it is of interest to note that the O(12)···H(26) and C(26)···O(12) distances are 2.294 and 3.222 Å, respectively, in the AM1 optimized structure.

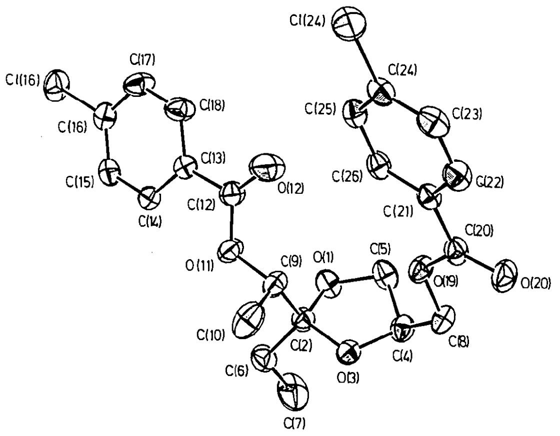


Fig. 1. Structure of (3) in the solid state. Displacement ellipsoids are plotted at 30% probability.

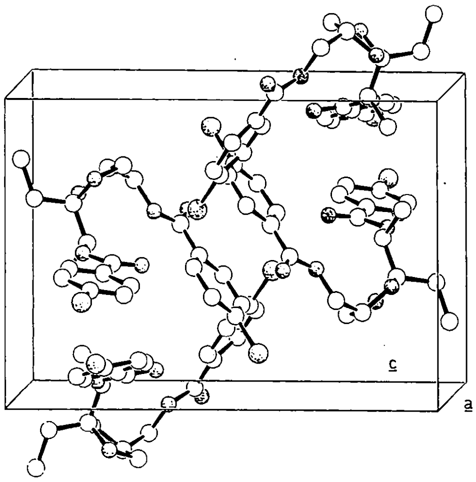


Fig. 2. Packing of (3) in the unit cell.

Determination of the most probable gas-phase structure of a molecule with such a high number of degrees of freedom like (3), obviously requires more sophisticated methods than a single quantum-chemical geometry optimization. While a molecular-dynamics study might be the appropriate approach in this regard, it is nevertheless interesting to note that the main structural features of (3) in the solid state also characterize a local minimum of the free isolated molecule.

Experimental

Reduction of (1) with $LiAlH_4$ in diethyl ether (Et_2O) yields (*RS*)-1-[(*RS*)-2-ethyl-*c*-4-hydroxymethyl-1,3-dioxolan-*r*-2-yl]ethanol, (2), which upon reaction with 4-chlorobenzoyl chloride in pyridine results in a racemic mixture of (3) in the form of colourless crystals (m.p. 355 K) (Berens, 1993). (3) was recrystallized from methanol.

Crystal data

$C_{22}H_{22}Cl_2O_6$
$M_r = 453.32$
Monoclinic
$P2_1/a$
$a = 12.171$ (2) Å
$b = 11.360$ (2) Å
$c = 16.118$ (4) Å
$\beta = 91.343$ (7)°
$V = 2227.98$ Å^3
$Z = 4$
$D_x = 1.351$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 10.12$–$19.33°$
$\mu = 0.3304$ mm^{-1}
$T = 293$ K
Irregular
$0.5 \times 0.4 \times 0.4$ mm
Colourless

Data collection

CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
5820 measured reflections
5342 independent reflections
3269 observed reflections [$I > 2\sigma(I)$]

$R_{int} = 0.0242$
$\theta_{max} = 28.8°$
$h = -15 \rightarrow 15$
$k = 0 \rightarrow 14$
$l = 0 \rightarrow 20$
3 standard reflections
frequency: 60 min
intensity variation: 6%

Refinement

Refinement on F
$R = 0.050$
$wR = 0.040$
$S = 2.627$
3269 reflections
272 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.3$ e Å^{-3}
$\Delta\rho_{\min} = -0.4$ e Å^{-3}

Extinction correction:
Zachariasen (1967); Larson (1970)
Extinction coefficient:
$r = 2997$ (308)
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)

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

	x	y	z	$U_{\rm eq}$
Cl(16)	1.28907 (5)	0.37312 (8)	0.80315 (5)	0.0885 (3)
Cl(24)	0.54589 (7)	0.13982 (7)	0.44318 (5)	0.0865 (3)
O(1)	0.6718 (1)	0.7101 (2)	0.8128 (1)	0.0650 (7)
O(3)	0.5079 (1)	0.6474 (1)	0.8605 (1)	0.0547 (6)
O(11)	0.7575 (1)	0.4800 (2)	0.8347 (1)	0.0648 (7)
O(12)	0.7579 (2)	0.4423 (3)	0.6996 (1)	0.114 (1)
O(19)	0.4313 (1)	0.5848 (1)	0.6919 (1)	0.0554 (6)
O(20)	0.2679 (1)	0.5745 (2)	0.6256 (1)	0.0729 (7)
C(2)	0.6232 (2)	0.6269 (2)	0.8652 (1)	0.0504 (8)
C(4)	0.4830 (2)	0.7271 (2)	0.7945 (2)	0.0565 (9)
C(5)	0.5915 (2)	0.7448 (2)	0.7522 (2)	0.065 (1)
C(6)	0.6675 (2)	0.6464 (3)	0.9528 (2)	0.069 (1)
C(7)	0.6462 (3)	0.7691 (3)	0.9846 (2)	0.115 (2)
C(8)	0.3903 (2)	0.6818 (2)	0.7404 (2)	0.0599 (9)
C(9)	0.6398 (2)	0.5023 (2)	0.8326 (2)	0.0592 (9)
C(10)	0.5839 (2)	0.4075 (3)	0.8813 (2)	0.090 (1)
C(12)	0.8053 (2)	0.4522 (3)	0.7643 (2)	0.061 (1)
C(13)	0.9261 (2)	0.4325 (2)	0.7764 (1)	0.0496 (8)
C(14)	0.9792 (2)	0.4505 (2)	0.8518 (1)	0.0549 (9)
C(15)	1.0910 (2)	0.4329 (2)	0.8599 (2)	0.060 (1)
C(16)	1.1490 (2)	0.3976 (2)	0.7931 (2)	0.0570 (9)
C(17)	1.0973 (3)	0.3795 (3)	0.7181 (2)	0.075 (1)
C(18)	0.9859 (2)	0.3970 (3)	0.7101 (2)	0.073 (1)
C(20)	0.3603 (2)	0.5386 (2)	0.6357 (1)	0.0540 (9)
C(21)	0.4090 (2)	0.4403 (2)	0.5891 (1)	0.0480 (8)
C(22)	0.3412 (2)	0.3741 (3)	0.5373 (2)	0.061 (1)
C(23)	0.3820 (2)	0.2814 (3)	0.4926 (2)	0.066 (1)
C(24)	0.4927 (2)	0.2569 (2)	0.4991 (2)	0.0584 (9)
C(25)	0.5627 (2)	0.3227 (2)	0.5489 (1)	0.0559 (9)
C(26)	0.5202 (2)	0.4136 (2)	0.5944 (1)	0.0520 (8)

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

Cl(16)—C(16)	1.731 (2)	C(9)—C(10)	1.504 (4)
Cl(24)—C(24)	1.739 (3)	C(12)—C(13)	1.496 (3)
O(1)—C(2)	1.406 (3)	C(13)—C(18)	1.369 (4)
O(1)—C(5)	1.422 (3)	C(13)—C(14)	1.378 (3)
O(3)—C(2)	1.424 (3)	C(14)—C(15)	1.379 (4)
O(3)—C(4)	1.424 (3)	C(15)—C(16)	1.361 (4)
O(11)—C(12)	1.325 (3)	C(16)—C(17)	1.365 (4)
O(11)—C(9)	1.454 (3)	C(17)—C(18)	1.373 (4)
O(12)—C(12)	1.186 (3)	C(20)—C(21)	1.478 (3)
O(19)—C(20)	1.343 (3)	C(21)—C(22)	1.382 (3)
O(19)—C(8)	1.446 (3)	C(21)—C(26)	1.387 (3)
O(20)—C(20)	1.204 (3)	C(22)—C(23)	1.375 (4)
C(2)—C(6)	1.516 (3)	C(23)—C(24)	1.378 (4)
C(2)—C(9)	1.524 (4)	C(24)—C(25)	1.378 (4)
C(4)—C(8)	1.501 (3)	C(25)—C(26)	1.376 (4)
C(4)—C(5)	1.514 (4)	C(26)···O(12)	3.335 (3)
C(6)—C(7)	1.510 (5)		
C(2)—O(1)—C(5)	107.9 (2)	C(18)—C(13)—C(12)	118.8 (2)
C(2)—O(3)—C(4)	109.6 (2)	C(14)—C(13)—C(12)	122.2 (2)
C(12)—O(11)—C(9)	118.3 (2)	C(13)—C(14)—C(15)	120.2 (2)
C(20)—O(19)—C(8)	115.9 (2)	C(16)—C(15)—C(14)	119.8 (2)
O(1)—C(2)—O(3)	106.6 (2)	C(15)—C(16)—C(17)	120.5 (2)
O(1)—C(2)—C(9)	110.9 (2)	C(15)—C(16)—Cl(16)	120.0 (2)
O(3)—C(2)—C(6)	110.7 (2)	C(17)—C(16)—Cl(16)	119.4 (2)
O(3)—C(2)—C(9)	105.8 (2)	C(16)—C(17)—C(18)	119.7 (3)
C(6)—C(2)—C(9)	114.2 (2)	C(13)—C(18)—C(17)	120.8 (2)
O(3)—C(4)—C(8)	111.1 (2)	O(20)—C(20)—O(19)	122.9 (2)
O(3)—C(4)—C(5)	104.4 (2)	O(20)—C(20)—C(21)	124.8 (2)
C(8)—C(4)—C(5)	115.8 (2)	O(19)—C(20)—C(21)	112.3 (2)
O(1)—C(5)—C(4)	104.2 (2)	C(22)—C(21)—C(26)	119.1 (2)
C(7)—C(6)—C(2)	113.1 (2)	C(22)—C(21)—C(20)	118.5 (2)
O(19)—C(8)—C(4)	108.1 (2)	C(26)—C(21)—C(20)	122.4 (2)
O(11)—C(9)—C(10)	108.6 (2)	C(23)—C(22)—C(21)	121.0 (2)
O(11)—C(9)—C(2)	107.0 (2)	C(22)—C(23)—C(24)	118.7 (2)
C(10)—C(9)—C(2)	114.8 (2)	C(25)—C(24)—C(23)	121.6 (2)
O(12)—C(12)—O(11)	124.2 (2)	C(25)—C(24)—Cl(24)	118.9 (2)
O(12)—C(12)—C(13)	123.8 (2)	C(23)—C(24)—Cl(24)	119.4 (2)
O(11)—C(12)—C(13)	112.0 (2)	C(26)—C(25)—C(24)	118.9 (2)
C(18)—C(13)—C(14)	119.0 (2)	C(25)—C(26)—C(21)	120.7 (2)

The horizontal detector aperture and the ω-scan range varied as $(1.90 + 1.05\tan\theta)$ mm and $(0.80 + 0.35\tan\theta)^\circ$, respectively. Data were corrected for Lorentz and polarization effects. The structure was solved by means of direct methods as implemented in the *Xtal*2.6 program package (Hall & Stewart, 1989), employing *GENSIN* to generate structure invariant relationships and *GENTAN* for the tangent phasing procedure. Displacement parameters for C, O and Cl were refined anisotropically. The positions of all H atoms could be located in a difference Fourier map and were subjected to 20 cycles of isotropic refinement ($U_{\rm H}$ = 0.065 Å^2; damping factor 0.1), while they were kept fixed in the final refinement. Besides the routines mentioned above, only facilities of the *Xtal*2.6 program package were used for the crystallographic calculations, while the semi-empirical computations were performed using the *MOPAC* set of quantum-chemical routines (Stewart, 1989). All calculations were carried out on a local VAX 3100 workstation. Molecular drawings and cell plots were generated using *ORTEP* (Johnson, 1965).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SH1081). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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