Table 6. *Hydrogen-bonding geometry (Å, °) for (III)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H102···Cl	0.98 (3)	2.51 (3)	3.481 (2)	168 (2)
O5—H500···O6	0.82	2.30	2.731 (2)	114
N1—H101···O5^{i}	0.96 (3)	1.97 (3)	2.898 (3)	163 (3)
O5—H500···Cl^{ii}	0.82	2.37	3.000 (2)	134
O6—H600···Cl^{iii}	0.82	2.31	3.129 (2)	178

Symmetry codes: (i) $\frac{1}{2}+x, y, \frac{1}{2}-z$; (ii) $x-\frac{1}{2}, \frac{1}{2}-y, -z$; (iii) $\frac{1}{2}-x, y-\frac{1}{2}, z$.

For (I), the water H atom parameters were found from $\Delta\rho$ maps, and refined with constraints ($U_{\rm iso} = 1.3U_{\rm eq}$ of the parent O atom). The other H atoms had all parameters refined. For (II), H atoms were constrained to ride on the parent atoms using the *AFIX* option in *SHELXL*97 (Sheldrick, 1997). For (III), an idealized geometry was applied to the hydroxy H atoms and all parameters were refined for the other H atoms.

For all compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1989*a*); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1989*b*); program(s) used to solve structures: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structures: *SHELXL*97; molecular graphics: *ORTEX* (McArdle, 1995); software used to prepare material for publication: *PARST* (Nardelli, 1983*b*).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1324). Services for accessing these data are described at the back of the journal.

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2*H*-1-Benzopyrans. III. 4-Hydroxy-3-methoxycarbonyl-2-dimethoxyphosphoryl-2*H*-1-benzopyran†

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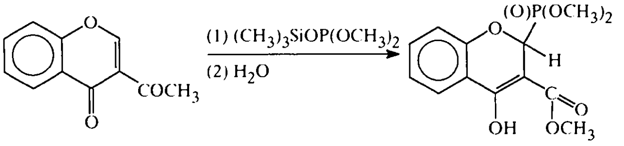
Abstract

The title compound, $C_{13}H_{15}O_7P$, consists of two condensed rings, namely, a pyranoid ring with an axially attached partially disordered dimethoxyphosphoryl group and a benzene ring. The conformation of the pyranoid ring is halfway between half-boat and half-chair, and the fusion of the rings does not exert significant influence on the planarity of the benzene ring.

Comment

This paper is a continuation of structural investigations on benzopyran derivatives (Olszak *et al.*, 1994, 1997). Since the 2*H*-1-benzopyran derivatives are known to exhibit spasmolytic effects (Kostka *et al.*, 1994), the title compound, (I), is expected to be pharmacologically active.



(I)

In (I), fusion with the pyranoid ring has no significant influence on the planarity of the benzene ring. The skeleton of the pyranoid ring itself shows a pseudo-twofold axis running through the midpoints of the C1—O1 and C3—C9 bonds [Δ_2(C1—O1) = 0.036 (1); Nardelli, 1983*a*]. Examination of the puckering parameters (Cremer & Pople, 1975) indicates an approximate half-chair conformation of the ring [Q_T = 0.323 (2) Å, Φ_2 = −137.5 (5)° and θ_2 = 116.9 (4)°, for the O1—C1—C2—C3—C9—C8 sequence].

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† Alternative name: methyl 2-dimethoxyphosphoryl-4-hydroxy-2*H*-1-benzopyran-3-carboxylate.

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The dimethoxyphosphoryl group is attached axially to the ring, the torsion angles C3—C2—C1—P10 and C8—O1—C1—P10 being 89.8 (2) and −85.3 (2)°, respectively. The O13 atom is distributed over two positions, with occupancy factors of 0.752 (6) and 0.248 (6). The disorder of the phosphoryl group involves the O13—C14 methoxy group which assumes two orientations defined by the torsion angles O1—C1—P10—O13*B* and O1—C1—P10—O13 of −34.7 (4) and −78.8 (2)°, respectively.

The hydroxyl group attached in position 4 interacts with the methoxycarbonyl group in position 3, forming a strong hydrogen bond [O30—H30 0.93 (4), O30···O16 2.591 (3), H30···O16 1.74 (4) Å and O30—H30···O16 151 (4)°] which closes an almost flat six-membered ring [maximum deviation from planarity is 0.039 (3) Å for C15 (H30 excluded)]. A weak C4—H4···O30 [H4···O3 2.47 (3) Å] interaction acts to keep the C2—C3—O30 moiety in the plane of the benzene ring, while a C1—H11···O17 [H11···O17 2.44 (3) Å] interaction determines the orientation of the O17—C18 methoxy group.

Comparison of bond lengths and angles of (I) with those of previously reported structures (Olszak *et al.*, 1994, 1997) does not show any significant differences.

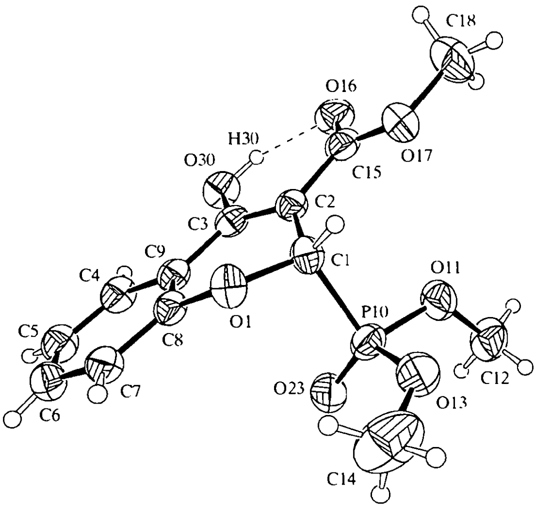

Fig. 1. *ORTEX* (McArdle, 1995) view of the title compound with the atomic numbering scheme (ellipsoids are at the 40% probability level).

Experimental

The title compound was prepared by reaction of methyl 4-oxo-4*H*-1-benzopyran-3-carboxylate with, initially, trimethylsilylolimethyl phosphite and then water according to the scheme in the *Comment*. The density of the compound was measured in carbon tetrachloride and tetralin.

Crystal data

$C_{13}H_{15}O_7P$
$M_r = 314.23$
Triclinic
$P\bar{1}$
$a = 9.0038 (6)$ Å
$b = 12.4130 (5)$ Å
$c = 6.6728 (8)$ Å
$\alpha = 96.458 (6)°$
$\beta = 99.231 (8)°$
$\gamma = 75.480 (4)°$
$V = 710.6 (1)$ Å^3
$Z = 2$
$D_x = 1.469$ Mg m^{-3}
$D_m = 1.466$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 30.95–41.46°$
$\mu = 2.023$ mm^{-1}
$T = 293 (2)$ K
Prism
0.2 × 0.1 × 0.1 mm
Light yellow

Data collection

Rigaku AFC-5*S* diffractometer
ω scans
Absorption correction: empirical ψ-scan correction (North *et al.*, 1968)
$T_{min} = 0.657$, $T_{max} = 0.817$
3831 measured reflections
2114 independent reflections

1778 reflections with $I > 2\sigma(I)$
$R_{int} = 0.015$
$\theta_{max} = 60.06°$
$h = -10 \rightarrow 10$
$k = -13 \rightarrow 13$
$l = -5 \rightarrow 7$
3 standard reflections every 150 reflections intensity decay: <2%

Refinement

Refinement on F^2
$R(F) = 0.047$
$wR(F^2) = 0.139$
$S = 1.231$
2112 reflections
226 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0964P)^2 + 0.0470P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.434$ e Å^{-3}
$\Delta\rho_{min} = -0.439$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.074 (5)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1—C1	1.444 (2)	C2—C15	1.444 (3)
O1—C8	1.373 (2)	C2—C3	1.348 (3)
C1—P10	1.828 (2)	C15—O16	1.237 (3)
C1—C2	1.498 (3)	C15—O17	1.322 (3)
P10—O11	1.552 (1)	O17—C18	1.446 (3)
P10—O23	1.423 (2)	C3—O30	1.343 (2)
O11—C12	1.425 (3)		
C1—O1—C8	116.4 (2)	O11—P10—O23	116.4 (1)
O1—C1—C2	113.3 (2)	P10—O11—C12	121.7 (2)
O1—C1—P10	106.9 (2)	C1—C2—C3	118.5 (2)
P10—C1—C2	112.8 (2)	C2—C3—O30	123.7 (2)
C1—P10—O23	115.1 (1)	O30—C3—C9	115.7 (2)
C1—P10—O11	101.0 (1)		

The H atoms of methyl groups were refined as rigid bodies and all parameters were refined for all other H atoms.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1989*a*). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEX* (McArdle, 1995). Software used to prepare material for publication: *PARST* (Nardelli, 1983*b*).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1323). Services for accessing these data are described at the back of the journal.

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4-Acetyl-4-methylheptanedinitrile at 173 K

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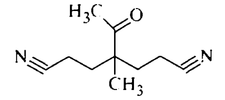
Abstract

The title compound, $C_{10}H_{14}N_2O$, serves as an precursor for ring-closure reactions to afford, for example, naphthyridines and quinolinediones. In the crystal, the molecule does not show any pre-organization favouring a ring closure; the heptanedinitrile chain is almost anti-peri-planar, with the C—C—C angles having nearly perfect tetrahedral values.

Comment

γ-Methylpimelonitrile and its derivatives can be used in cyclization reactions, with inorganic acids as catalysts, resulting in tetrahydropyridine derivates. Zondler & Pfleiderer (1972) showed that decahydro-1,8-naphthyridines can be synthesized, while Richtzenhain *et al.* (1966) synthesized substituted 2,3-dimethyl-3-(γ-aminopropyl)piperidine after reduction of the nitriles with Raney nickel and hydrogen. Koelsch & Walker (1950) found that Δ^8-octahydroquinoline-2,7-dione could be obtained by reaction with concentrated sulfuric acid at 393–413 K. We were interested in the question of whether the precursor of the above-mentioned reactions is predisposed towards ring closure. However, the crystal structure analysis revealed that all torsion angles of the heptanedinitrile chain are antiperiplanar. The molecule, (I), exhibits approximate non-crystallographic *m* symmetry. Atoms C1, C2, O2, C3 and C4 lie in a common plane (r.m.s. deviation = 0.001 Å) and the torsion angles of the remaining atoms have similar absolute values, differing only in sign.



(I)

Bond lengths and angles in (I) do not show unusual values. There were no additional crystallographic data for similar compounds in the Cambridge Structural Database (Allen & Kennard, 1993).

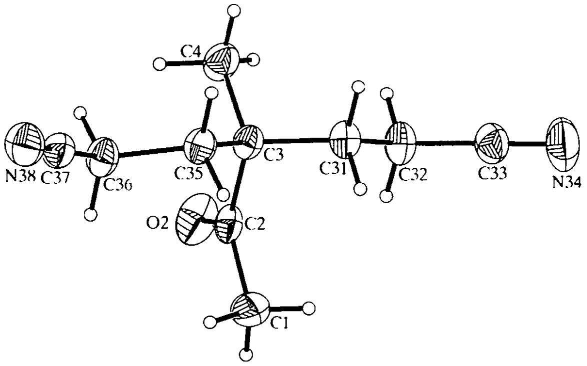


Fig. 1. Perspective view of the title compound with the atom numbering; displacement ellipsoids are at the 50% probability level.

Experimental

The title compound was obtained by dissolving 2-butanone (0.1 mol) in *tert*-butanol (20 ml) and adding this solution dropwise to 30% methanolic KOH (0.5 ml) with stirring and ice cooling. Afterwards, acrylonitrile (0.2 mol) in *tert*-butanol (20 ml) was added dropwise to the reaction mixture while keeping the temperature of the mixture under 263 K, and the resulting mixture stirred for 30 min. Petroleum ether (10 ml) was then added and the precipitate filtered off. Suitable crystals were obtained by recrystallization from petroleum ether.