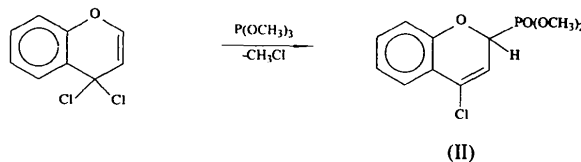
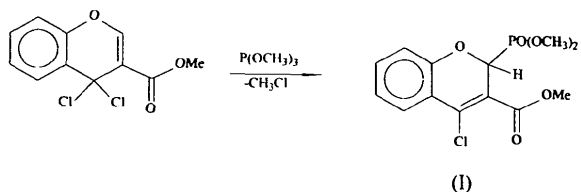


- Duax, W. L., Weeks, C. M. & Rohrer, D. C. (1976). *Topics in Stereochemistry*, Vol. 9, edited by E. L. Eliel & N. Allinger, pp. 271–383. New York: John Wiley.
- Frenz, B. A. (1978). *The Enraf-Nonius CAD-4 SDP – a Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution. Computing in Crystallography*, edited by H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi, pp. 64–71. Delft University Press.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Nardelli, M. (1983). *Comput. Chem.* 7, 95–98.
- Sheldrick, G. M. (1990). *Acta Cryst.* A46, 467–473.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Sivaraman, J., Subramanian, K., Velmurugan, D., Subramanian, E. & Shanmugasundaram, P. (1996). *Acta Cryst.* C52, 481–483.

show biological activity (Farkas, Kallay, Gabor & Wagner, 1982; Gabor, 1988; Yudelevich, Komarov & Ionin, 1985). The title compounds exhibit either a myocardial nutritional circulation effect in rabbits and a spasmolytic effect on isolated rabbit intestine (Kostka, Modranka, Szadowska, Graczyk & Orszulak, 1994) or are expected to exhibit spasmolytic properties.



Acta Cryst. (1997). C53, 1514–1516

2H-1-Benzopyrans. II. 4-Chloro-3-methoxy-carbonyl-2-dimethoxyphosphoryl-2H-1-benzopyran, (I), and 4-Chloro-2-dimethoxyphosphoryl-2H-1-benzopyran, (II)†

TOMASZ A. OLSZAK,^a MIECZYSLAW J. GRABOWSKI,^a ANDRZEJ STĘPIEK,^a R. MODRANKA^b AND K. KOSTKA^b

^aDepartment of Crystallography, University of Lodz, Pomorska 149/153, PL-92236 Łódź, Poland, and ^bInstitute of Chemistry, Faculty of Pharmacy, Medical University, Muszyńskiego 1, PL-90151 Łódź, Poland. E-mail: crystal@krysia.uni.lodz.pl

(Received 13 October 1995; accepted 15 May 1997)

Abstract

The pyranoid rings are in a half-boat conformation in compound (I), C₁₃H₁₄ClO₆P, and in a deformed half-boat-towards-half-chair conformation in compound (II), C₁₁H₁₂ClO₄P. Fusion with the pyranoid ring has no significant influence on the planarity of the benzene ring in either compound. In both structures, the dimethoxyphosphoryl group is attached axially. The presence of the methoxycarbonyl substituent in (I) seems responsible for the disorder observed in the dimethoxyphosphoryl group.

Comment

This paper is the continuation of the structure determinations of new derivatives of benzopyran (Olszak *et al.*, 1994). It is known that 2H-1-benzopyran derivatives

† Alternative names: methyl 4-chloro-2-dimethoxyphosphoryl-2H-1-benzopyran-3-carboxylate, (I), and dimethyl (4-chloro-2H-1-benzopyran-2-yl)phosphonate, (II).

The condensed ring system in (I), excepting atom C1, is almost planar. The best plane calculated through the benzene ring and that through the five atoms of the pyranoid ring form a dihedral angle of 0.50 (7)°. The benzene ring is planar to within experimental error. The pyranoid ring has a half-boat conformation. The puckering parameters (Cremer & Pople, 1975) corresponding to the sequence O1—C1—C2—C3—C9—C8 are $Q = 0.364$ (2) Å, $\varphi = 41.8$ (4)° and $\theta_2 = 64.6$ (4)°, with C1 at the apex. A pseudosymmetry twofold axis runs through the midpoints of the O1—C1 and C3—C9 bonds [asymmetry parameter $\Delta_2(\text{C1—O1}) = 0.039$ (1); Nardelli, 1983]. The dimethoxyphosphoryl group is attached axially to the ring with torsion angles C8—O1—C1—P10 and C3—C2—C1—P10 of 81.2 (2) and –89.1 (2)°, respectively. The group is disordered, with atoms O13 and O23 split over two sites with occupation factors $k_A = 0.709$ (7) and $k_B = 0.291$ (7).

The pyranoid ring in compound (II) is in a half-chair conformation that is slightly deformed towards a half-boat conformation, with the C1 atom at the apex. The skeleton of the pyranoid ring itself has a twofold pseudosymmetry axis running through the midpoints of the C1—O1 and C3—C9 bonds. The puckering parameters (Cremer & Pople, 1975) corresponding to the sequence C1—C2—C3—C9—C8—O1 are $Q = 0.194$ (2) Å, $\varphi_2 = 151.2$ (9)° and $\theta_2 = 116.0$ (7)°, and the asymmetry parameter (Nardelli, 1983) $\Delta_2(\text{C1—O1})$ is 0.002 (1)°. The dimethoxyphosphoryl group is attached axially to the ring. The torsion angles C8—O1—C1—P10 and C3—C2—C1—P10 are 102.2 (2) and –110.6 (3)°, respectively.

Compound (II) is devoid of a methoxycarbonyl group in position 3 in comparison with (I). This absence seems to influence the conformation of the dimethoxy-

phosphoryl group. Indeed, two O atoms of the three in the dimethoxyphosphoryl group of compound (I) were found to be disordered over two possible positions. The presence of the methoxycarbonyl group influences the total puckering amplitude of the pyranoid ring, which in (I) is approximately double that in (II). The distances and angles in (II) are in good agreement with those in the substituted compound (I).

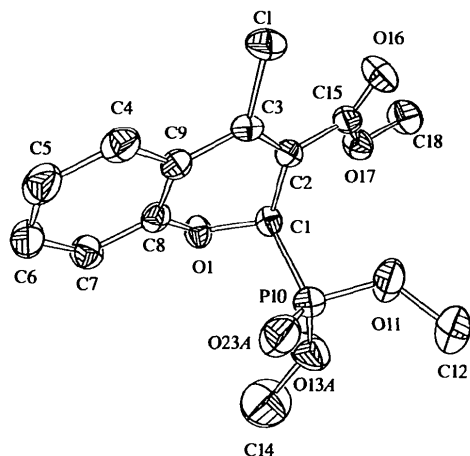


Fig. 1. The atomic numbering scheme of compound (I) [only major occupancy atoms are shown; site occupancy (A) 0.709 (7)]. Displacement ellipsoids are drawn at the 40% probability level.

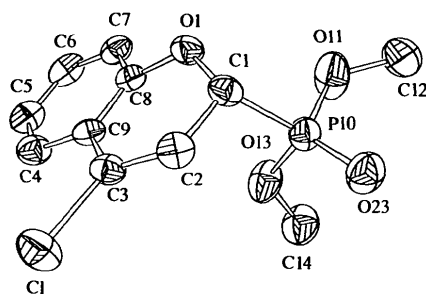


Fig. 2. The atomic numbering scheme of compound (II). Displacement ellipsoids are drawn at the 40% probability level.

Experimental

Compound (I) was obtained by the reaction of 4,4-dichloro-3-methoxycarbonyl-4*H*-1-benzopyran (Föhlisch, 1971) with trimethyl phosphite (Modranka, 1995). The light-yellow prismatic crystals were obtained by slow evaporation from benzene or diethyl ether solution at room temperature. Compound (II) was obtained by the reaction of 4,4-dichloro-4*H*-1-benzopyran (Föhlisch, 1971) with trimethyl phosphite (Modranka & Kostka, 1997). The light-yellow crystals were obtained by slow evaporation from diethyl ether solution at room temperature.

Compound (I)

Crystal data

$C_{13}H_{14}ClO_6P$
 $M_r = 332.68$

Cu $K\alpha$ radiation
 $\lambda = 1.54178 \text{ \AA}$

Triclinic

$P\bar{1}$

$a = 9.035 (1) \text{ \AA}$

$b = 12.501 (1) \text{ \AA}$

$c = 6.9634 (5) \text{ \AA}$

$\alpha = 96.62 (1)^\circ$

$\beta = 102.08 (1)^\circ$

$\gamma = 73.56 (1)^\circ$

$V = 736.3 (1) \text{ \AA}^3$

$Z = 2$

$D_x = 1.5006 \text{ Mg m}^{-3}$

$D_m = 1.490 \text{ Mg m}^{-3}$

D_m measured by flotation

Data collection

Rigaku AFC-5S four-circle diffractometer

ω scans

Absorption correction: empirical ψ scan (North, Phillips & Mathews, 1968)

$T_{\min} = 0.587$, $T_{\max} = 0.700$

4374 measured reflections

2187 independent reflections

Cell parameters from 22 reflections

$\theta = 28.81\text{--}41.59^\circ$

$\mu = 3.564 \text{ mm}^{-1}$

$T = 293 (2) \text{ K}$

Prism

$0.2 \times 0.2 \times 0.1 \text{ mm}$

Light yellow

1653 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.015$

$\theta_{\max} = 60.08^\circ$

$h = -10 \rightarrow 10$

$k = -14 \rightarrow 14$

$l = -7 \rightarrow 7$

3 standard reflections every 150 reflections intensity decay: $<2\%$

Refinement

Refinement on F^2

$R(F) = 0.033$

$wR(F^2) = 0.090$

$S = 1.195$

2183 reflections

239 parameters

Methyl H atoms refined as rigid body, other H atoms refined isotropically

$w = 1/[\sigma^2(F_o^2) + (0.0537P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = -0.228$

$\Delta\rho_{\max} = 0.272 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.320 \text{ e \AA}^{-3}$

Extinction correction:

SHELXL93 (Sheldrick, 1993)

Extinction coefficient:

0.0062 (7)

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$) for (I)

O1—C1	1.442 (2)	C3—C1	1.725 (2)
O1—C8	1.375 (2)	C9—C8	1.393 (3)
C1—C2	1.509 (3)	C15—O16	1.197 (3)
C1—P10	1.822 (2)	C15—O17	1.338 (3)
C2—C3	1.339 (3)	O17—C18	1.448 (3)
C2—C15	1.483 (3)	P10—O11	1.544 (1)
C3—C9	1.461 (2)	O11—C12	1.431 (4)
C1—O1—C8	115.3 (2)	C3—C9—C8	117.5 (2)
O1—C1—P10	108.9 (2)	C8—C9—C4	117.6 (2)
O1—C1—C2	113.4 (2)	O1—C8—C9	121.4 (2)
C2—C1—P10	112.1 (2)	C9—C8—C7	121.5 (2)
C1—C2—C15	118.4 (2)	O1—C8—C7	117.0 (2)
C1—C2—C3	116.6 (2)	C2—C15—O17	110.8 (2)
C3—C2—C15	125.0 (2)	C2—C15—O16	125.8 (2)
C2—C3—C1	122.6 (2)	O16—C15—O17	123.4 (3)
C2—C3—C9	121.3 (2)	C15—O17—C18	115.6 (2)
C9—C3—C1	116.0 (2)	P10—O11—C12	122.6 (2)
C3—C9—C4	124.8 (2)		

Compound (II)

Crystal data

$C_{11}H_{12}ClO_4P$
 $M_r = 274.64$

Cu $K\alpha$ radiation
 $\lambda = 1.54178 \text{ \AA}$

Triclinic
 $P\bar{1}$
 $a = 7.8864$ (5) Å
 $b = 11.3138$ (10) Å
 $c = 7.2675$ (6) Å
 $\alpha = 108.444$ (7)°
 $\beta = 92.736$ (7)°
 $\gamma = 82.800$ (7)°
 $V = 610.26$ (8) Å³
 $Z = 2$
 $D_x = 1.4946$ Mg m⁻³
 D_m not measured

Data collection

Rigaku AFC-5S diffractometer
 ω scans
 Absorption correction: empirical ψ scan (North, Phillips & Mathews, 1968)
 $T_{\min} = 0.898$, $T_{\max} = 1.000$
 1915 measured reflections
 1791 independent reflections

Refinement

Refinement on F^2
 $R(F) = 0.033$
 $wR(F^2) = 0.088$
 $S = 1.082$
 1791 reflections
 185 parameters
 Methoxy H atoms refined as rigid body with fixed displacement parameters, other H atoms refined isotropically
 $w = 1/[\sigma^2(F_o^2) + (0.0571P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

Cell parameters from 23 reflections
 $\theta = 22.72$ – 34.09 °
 $\mu = 0.0410$ mm⁻¹
 $T = 293$ (2) K
 Prism
 $0.2 \times 0.1 \times 0.1$ mm
 Light yellow

1384 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.014$
 $\theta_{\text{max}} = 60.07$ °
 $h = 0 \rightarrow 8$
 $k = -12 \rightarrow 12$
 $l = -8 \rightarrow 8$
 3 standard reflections every 200 reflections
 intensity decay: <2%

$(\Delta/\sigma)_{\text{max}} = 0.008$
 $\Delta\rho_{\text{max}} = 0.252$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.186$ e Å⁻³
 Extinction correction: *SHELXL93* (Sheldrick, 1993)
 Extinction coefficient: 0.0140 (12)
 Scattering factors from *International Tables for Crystallography* (Vol. C)

C1—C2—C3	121.1 (2)	C1—P10—O11	104.6 (1)
C2—C3—C1	119.9 (2)	C1—P10—O23	113.4 (1)
C2—C3—C9	121.5 (2)	O11—P10—O13	105.0 (1)
C9—C3—C1	118.6 (2)	O23—P10—O13	115.6 (1)
C3—C9—C4	125.2 (2)	O23—P10—O11	115.2 (1)
C3—C9—C8	116.6 (2)	P10—O11—C12	126.1 (2)
C8—C9—C4	118.2 (2)	P10—O13—C14	121.5 (2)

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1989); program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *OR-TEX* (McArdle, 1995); software used to prepare material for publication: *PARST* (Nardelli, 1993).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1207). Services for accessing these data are described at the back of the journal.

References

- Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
 Farkas, L., Kallay, F., Gabor, M. & Wagner, H. (1982). *Flavonoids and Bioflavonoids*, edited by Akademiai Kiado (Budapest), pp. 363–401. Amsterdam: Elsevier.
 Föhlich, B. (1971). *Chem. Ber.* **104**, 350–351.
 Gabor, M. (1988). In *The Pharmacology of Benzopyrone Derivatives and Related Compounds*, edited by Akademiai Kiado (Budapest). Amsterdam: Elsevier.
 Kostka, K., Modranka, R., Szadowska, A., Graczyk, J. & Orszulak, D. (1994). *Eur. J. Pharm. Sci.* **2**, 143.
 McArdle, P. (1995). *J. Appl. Cryst.* **28**, 65.
 Modranka, R. (1995). Dissertation. Medical University, Łódź, Poland.
 Modranka, R. & Kostka, K. (1997). In preparation.
 Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
 Molecular Structure Corporation (1989). *TEXSAN. TEXRAY Structure Analysis Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
 Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
 Nardelli, M. (1993). *PARST. A System of Computer Routines for Calculating Molecular Parameters from Results of Crystal Structure Analyses*. University of Parma, Italy.
 North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
 Olszak, T. A., Stępień, A., Renz, M., Grabowski, M. J., Kostka, K. & Modranka, R. (1994). *Acta Cryst.* **C50**, 284–286.
 Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
 Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
 Yudelevich, V. I., Komarov, E. V. & Ionin, B. I. (1985). *Khim. Farm. Zh.* **19**, 668–685.

Table 2. Selected geometric parameters (Å, °) for (II)

O1—C1	1.429 (2)	C9—C4	1.393 (4)
O1—C8	1.370 (3)	C8—C7	1.384 (3)
C1—C2	1.487 (3)	P10—O23	1.453 (1)
C1—P10	1.817 (2)	P10—O11	1.550 (2)
C2—C3	1.318 (3)	P10—O13	1.568 (2)
C3—C9	1.461 (3)	O11—C12	1.403 (3)
C3—C1	1.734 (2)	O13—C14	1.420 (3)
C9—C8	1.391 (3)		
C1—O1—C8	119.5 (2)	O1—C8—C9	122.6 (2)
O1—C1—P10	111.6 (2)	C9—C8—C7	121.0 (2)
O1—C1—C2	114.5 (2)	O1—C8—C7	116.3 (2)
C2—C1—P10	110.8 (2)	C1—P10—O13	101.5 (1)