N1	0.6543 (2)	0.3874 (2)	−0.2993 (2)	0.0444 (8)
C100	0.6588 (2)	0.3000 (2)	−0.2530 (2)	0.0516 (11)
C110	0.5755 (3)	0.2562 (3)	−0.2744 (5)	0.084 (2)
C120	0.7339 (3)	0.2580 (3)	−0.3105 (3)	0.0694 (15)
C130	0.6777 (3)	0.3049 (3)	−0.1273 (3)	0.0695 (16)
C1	0.6460 (3)	0.3912 (2)	−0.4253 (2)	0.0523 (11)
C8	0.6311 (2)	0.4749 (2)	−0.4681 (2)	0.0446 (10)
C9	0.6090 (2)	0.5393 (2)	−0.4007 (2)	0.0467 (19)
C6	0.5996 (2)	0.5263 (2)	−0.2757 (2)	0.0519 (11)
O6	0.6763 (2)	0.5575 (2)	−0.2251 (2)	0.0645 (19)
C7	0.5858 (2)	0.4392 (2)	−0.2473 (3)	0.0532 (12)
C2	0.6406 (2)	0.4879 (2)	−0.5834 (2)	0.0492 (10)
O2	0.6582 (2)	0.4215 (2)	−0.6469 (2)	0.0622 (19)
C3	0.6320 (2)	0.5635 (3)	−0.6280 (3)	0.0594 (13)
C4	0.6130 (2)	0.6278 (2)	−0.5596 (3)	0.0609 (12)
O4	0.6082 (2)	0.7020 (2)	−0.6080 (3)	0.0929 (13)
C5	0.5988 (2)	0.6158 (2)	−0.4454 (3)	0.0571 (12)
O500	0.5301 (2)	0.4330 (2)	0.0586 (2)	0.0822 (10)
O600	0.4121 (2)	0.1760 (2)	0.4543 (4)	0.1315 (17)

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

S100—O101	1.462 (2)	C100—C130	1.526 (4)
S100—O102	1.460 (3)	O500—H501	1.081 (4)
N1—C1	1.506 (3)	O6—O101	2.679 (3)
N1—C7	1.503 (5)	H600—O101	1.86 (4)
N1—C100	1.552 (5)	O500—H501	1.081 (4)
C1—C8	1.496 (5)	O500—O102	2.827 (4)
C2—C3	1.368 (6)	H501—O102	1.755 (4)
C2—C8	1.396 (3)	N1—H100	0.86 (3)
C2—O2	1.363 (4)	N1—O6^{i}	2.928 (4)
C3—C4	1.373 (6)	H100—O6^{i}	2.08 (3)
C4—C5	1.391 (5)	O4—H400	0.78 (4)
C4—O4	1.360 (5)	O4—O600^{ii}	2.745 (5)
C5—C9	1.384 (5)	H400—O600^{ii}	2.00 (4)
C6—C7	1.499 (5)	O2—H200	0.84 (5)
C6—C9	1.510 (3)	O2—O102^{iii}	2.640 (3)
C6—O6	1.434 (4)	H200—O102^{iii}	1.83 (5)
C8—C9	1.379 (4)	O600—H602	1.081 (5)
C100—C110	1.508 (6)	O600—O101^{iv}	2.748 (4)
C100—C120	1.523 (6)	H200—O102^{v}	3.32 (5)
O101—S100—O102	109.2 (1)	C6—C7—N1	110.9 (3)
O101—S100—O101^{i}	108.8 (1)	C1—C8—C2	117.5 (3)
O102—S100—O102^{i}	109.9 (1)	C1—C8—C9	124.0 (2)
O101—S100—O102^{i}	109.8 (1)	C2—C8—C9	118.6 (3)
O102—S100—O101^{i}	109.9 (1)	C5—C9—C6	119.9 (3)
C1—N1—C7	109.0 (3)	C5—C9—C8	121.0 (3)
C1—N1—C100	113.4 (3)	C6—C9—C8	119.1 (3)
C7—N1—C100	114.8 (3)	N1—C100—C110	110.6 (3)
N1—C1—C8	113.0 (2)	N1—C100—C120	107.6 (3)
C3—C2—C8	120.8 (3)	N1—C100—C130	107.9 (3)
C3—C2—O2	123.0 (3)	C110—C100—C120	111.4 (3)
C8—C2—O2	116.2 (3)	C110—C100—C130	110.9 (3)
C2—C3—C4	120.2 (3)	C120—C100—C130	108.4 (3)
C3—C4—C5	120.1 (3)	O6—H600—O101	165 (4)
C3—C4—O4	117.6 (3)	O500—H501—O102	170.8 (3)
C5—C4—O4	122.3 (3)	N1—H100—O6^{i}	168 (3)
C4—C5—C9	119.2 (3)	O4—H400—O600^{ii}	161 (4)
C7—C6—C9	111.9 (2)	O2—H200—O102^{iii}	163 (5)
C7—C6—O6	111.9 (2)	O600—H602—O101^{iv}	152.9 (4)
C9—C6—O6	106.3 (3)		
C1—C8—C2—02	3.4 (4)	C100—N1—C7—C6	166.3 (3)
C1—C8—C2—C3	−176.9 (3)	O6—C6—C7—N1	−66.6 (3)
C1—C8—C9—C6	0.5 (5)	C7—N1—C1—C8	43.9 (4)
C1—C8—C9—C5	177.9 (3)	C7—N1—C100—C110	60.9 (4)
C8—C9—C6—C7	−20.1 (4)	C7—N1—C100—C120	−177.3 (3)
C8—C9—C6—O6	102.3 (3)	C7—N1—C100—C130	−60.5 (4)
C9—C6—C7—N1	52.7 (3)	N1—C1—C8—C9	−13.1 (5)
C1—N1—C7—C6	−65.4 (3)	N1—C1—C8—C2	166.7 (3)

Symmetry codes: (i) $1-x, 1-y, z$; (ii) $1-x, 1-y, -z$; (iii) $x, y, z-1$; (iv) $1-x, y, -z$; (v) $\frac{3}{2}-x, 1-y, z-1$.

The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1985). The *E* map revealed the positions of all the non-H atoms. Refinement was by least squares using *SHELX*76 (Sheldrick, 1976) of the *CRULER* package (Rizzoli, Sangermano, Calestani & Andreetti, 1986) with isotropic and then anisotropic temperature factors. H atoms were located on a difference Fourier map. The H atoms of the water molecules (H501, H502, H601, H602) were refined as components of a rigid body.

This work was supported by project R. P. II.10 from the Polish Ministry of National Education.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71437 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU1042]

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2*H*-1-Benzopyrans. I. (*E*)-4-Chloro-2-[dimethoxyphosphoryl(dimethoxyphosphoryloxy)methylene]-2*H*-1-benzopyran

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Abstract

The title molecule, $C_{14}H_{17}ClO_8P_2$, consists of two six-membered condensed rings, with a Cl atom at position 4 and a dimethoxyphosphoryl(dimethoxyphosphoryloxy)methylene group at position 2. Both rings are aromatic. The best planes of the two rings

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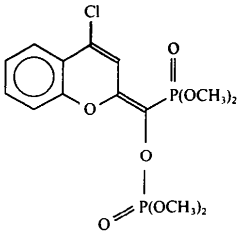
form a dihedral angle of 178.5 (1)°. The Cl atom lies 0.012 (2) Å out of the plane defined by the ring. The molecule is the *E* isomer. The torsion angle O4—C3—C11—P19 is −174.2 (2)°.

Comment

This paper commences reports on the structures of new derivatives of benzopyran. This group of compounds is interesting because of their biological activity (Farkas, Kallay, Gabor & Wagner, 1982; Bergmann & Gericke, 1990; Gericke, Harting, Lues & Schittenhelm, 1991). The title compound (I) was obtained by the reaction of 4,4-dichloro-4*H*-1-benzopyran-2-carbonyl chloride (Zagorevskii & Zykov, 1960) with trimethylphosphite (Kostka, Modranka, Grabowski & Stępień, 1993). The ^{31}P NMR (δ ^{31}P NMR and J_{PP}) spectra showed that the two stereoisomers (*E* and *Z*) were obtained. The *Z* isomer is thermodynamically labile and rapidly undergoes transition to the *E* isomer.



(I)

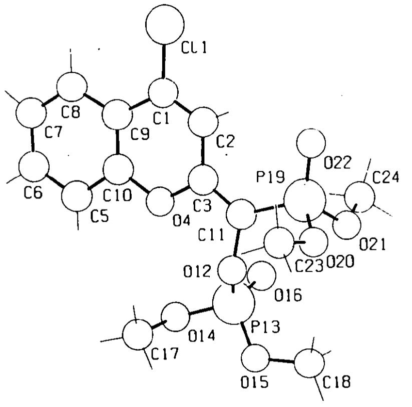


Fig. 1. View of the title compound with the atom-numbering scheme.

Experimental

Crystal data

$C_{14}H_{17}ClO_8P_2$
M_r = 410.7
Orthorhombic
Pbca
a = 16.748 (1) Å
b = 27.619 (3) Å
c = 7.962 (1) Å
V = 3682.9 (7) Å^3
Z = 8
D_x = 1.4813 (2) Mg m^{-3}
D_m = 1.472 Mg m^{-3}
D_m measured by flotation

Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 25 reflections
θ = 18.0–49.1°
μ = 3.89 mm^{-1}
Room temperature
Thick tabular
0.3 × 0.2 × 0.1 mm
Light yellow
Crystal source: slow evaporation from diethyl ether

Data collection

Kuma KM4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
8414 measured reflections
3763 independent reflections
3059 observed reflections [$I > 3\sigma(I)$]
$R_{\rm int}$ = 0.032

$\theta_{\rm max}$ = 80.0°
$h = -21 \rightarrow 21$
$k = -35 \rightarrow 0$
$l = -9 \rightarrow 0$
3 standard reflections monitored every 100 reflections
intensity variation: none

Refinement

Refinement on F
R = 0.049
wR = 0.0451
S = 1.41
3059 reflections
267 parameters
Unit weights applied
$(\Delta/\sigma)_{\rm max}$ = 0.23

$\Delta\rho_{\rm max}$ = 0.48 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.60 e Å^{-3}
Atomic scattering factors from *CRULER* (Rizzoli, Sangermano, Calestani & Andreetti, 1986)

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

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

	x	y	z	$U_{\rm eq}$
Cl1	0.0378 (1)	0.2027	−0.1714 (2)	0.1055 (5)
C1	0.1050 (2)	0.2475 (1)	−0.1169 (5)	0.0613 (12)
C2	0.0842 (2)	0.2933 (1)	−0.1312 (5)	0.569 (12)
C3	0.1389 (2)	0.3318 (1)	−0.0888 (4)	0.463 (10)
O4	0.2127 (1)	0.3187 (1)	−0.0314 (3)	0.584 (7)
C5	0.3096 (3)	0.2621 (2)	0.0510 (7)	0.0829 (19)
C6	0.3344 (3)	0.2150 (2)	0.0698 (8)	0.104 (2)
C7	0.2863 (4)	0.1776 (2)	0.0249 (8)	0.102 (2)
C8	0.2106 (3)	0.1858 (1)	−0.0380 (7)	0.0808 (17)
C9	0.1827 (2)	0.2334 (1)	−0.0566 (5)	0.0599 (13)
C10	0.2337 (2)	0.2705 (1)	−0.0132 (5)	0.0597 (12)
C11	0.1250 (2)	0.3794 (1)	−0.0994 (4)	0.0432 (9)
O12	0.1883 (1)	0.4120 (1)	−0.0703 (3)	0.0444 (7)
P13	0.2232	0.4258	0.1090 (1)	0.0466 (3)
O14	0.3060 (1)	0.4004 (1)	0.1246 (3)	0.0611 (9)
C17	0.3613 (2)	0.3987 (2)	−0.0144 (5)	0.0741 (15)
O15	0.2475 (1)	0.4795 (1)	0.0808 (3)	0.0663 (9)
C18	0.1867 (3)	0.5161 (1)	0.0575 (7)	0.0940 (19)
O16	0.1714 (1)	0.4152 (1)	0.2487 (3)	0.0636 (9)
P19	0.0340	0.4092	−0.1512 (1)	0.0493 (2)
O20	0.0567 (1)	0.4511 (1)	−0.2750 (3)	0.0656 (9)
C23	0.0919 (2)	0.4401 (2)	−0.4337 (5)	0.0787 (15)
O21	0.0132 (1)	0.4430 (1)	−0.0001 (3)	0.0617 (8)
C24	−0.0218 (2)	0.4223 (2)	0.1494 (5)	0.0789 (15)
O22	−0.0280 (1)	0.3755 (1)	−0.2035 (4)	0.0704 (9)

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

Cl1—C1	1.728 (3)	C1—C2	1.317 (4)
C1—C9	1.441 (5)	C2—C3	1.444 (4)
C3—O4	1.367 (4)	C3—C11	1.338 (4)

O4—C10	1.385 (4)	C5—C6	1.374 (8)
C5—C10	1.390 (6)	C6—C7	1.358 (8)
C7—C8	1.382 (8)	C8—C9	1.403 (4)
C9—C10	1.378 (4)	C11—P19	1.781 (3)
C11—O12	1.410 (4)	O12—P13	1.589 (2)
P13—O14	1.559 (2)	P13—O15	1.554 (3)
P13—O16	1.441 (2)	O14—C17	1.444 (4)
O15—C18	1.447 (5)	P19—O20	1.567 (3)
P19—O21	1.562 (3)	P19—O22	1.455 (2)
O20—C23	1.427 (5)	O21—C24	1.445 (5)
C2—C1—C9	121.8 (3)	C2—C1—Cl1	119.6 (3)
C9—C1—Cl1	118.6 (2)	C1—C2—C3	121.3 (3)
C2—C3—O4	117.2 (3)	C2—C3—C11	126.8 (3)
C11—C3—O4	116.0 (3)	C3—O4—C10	121.3 (3)
C6—C5—C10	118.3 (5)	C5—C6—C7	120.8 (5)
C6—C7—C8	121.0 (5)	C7—C8—C9	119.8 (4)
C1—C9—C8	126.1 (3)	C1—C9—C10	116.3 (3)
C8—C9—C10	117.6 (3)	C5—C10—O4	115.6 (3)
C5—C10—C9	122.4 (3)	C9—C10—O4	122.1 (3)
C3—C11—O12	119.1 (3)	C3—C11—P19	128.2 (2)
O12—C11—P19	112.7 (2)	C11—O12—P13	125.3 (2)
O12—P13—O14	106.9 (1)	O12—P13—O15	101.3 (1)
O12—P13—O16	115.1 (1)	O14—P13—O15	102.0 (1)
O14—P13—O16	112.5 (1)	O15—P13—O16	117.6 (1)
C17—O14—P13	121.6 (2)	C18—O15—P13	120.1 (2)
C11—P19—O20	106.2 (1)	C11—P19—O21	106.8 (1)
C11—P19—O22	112.4 (1)	O20—P19—O21	95.6 (1)
O20—P19—O22	117.7 (1)	O21—P19—O22	116.3 (1)
C23—O20—P19	120.0 (3)	C24—O21—P19	119.2 (3)

The structure was solved by Patterson and direct methods using *SHELXS*86 (Sheldrick, 1985). The first *E* map revealed six atoms, three of which were Cl and P atoms. Calculation of the Fourier map with these atoms revealed all of the non-H atoms. Least-squares refinement was carried out using *SHELX*76 (Sheldrick, 1976) of the *CRULER* package (Rizzoli, Sangermano, Calestani & Andreetti, 1986) with isotropic and then anisotropic temperature factors. H atoms were located on a difference Fourier map and the methyl H atoms were refined as part of a rigid body.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and geometry, least-squares-planes data and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71438 (25 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU1041]

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Structure of 5-[(1-Amidiniohydrazono)ethyl]-4-methyl-2-methylthio-3H^+-pyrimidinium Dichloride Hydrate, $C_9H_{16}N_6S^{2+}.2Cl^-.H_2O$

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Abstract

The amidiniohydrazone group of the title compound (5-acetyl-4-methyl-2-methylthiopyrimidine amidinohydrazone dihydrochloride) has a *trans* conformation (*E*) and the (amidiniohydrazone)ethyl part of the molecule compares very well with the same chaining in mitoguazone and its analogue. Both ionic salts are stabilized by a series of hydrogen bonds to both water molecules and chlorine ions. The structure consists of stacks of parallel planes of the dipositive ion.

Comment

The hydrochloride salt of the amidinohydrazone of 5-acetyl-4-methyl-2-methylthiopyrimidine (3) is the likely intermediary in the reaction of transformation of 5-acetyl-4-methyl-2-methylthiopyrimidine (1) into 4-acetyl-1-amidino-3-methylpyrazole amidinohydrazone dihydrochloride (2) by action of aminoguanidine hydrochloride (a.g. HCl) in acidic boiling methanol (Menichi, Naciri, Kokel & Hubert-Habart, 1984; Menichi, Boutar, Kokel, Takagi & Hubert-Habart, 1986; Bajnati & Hubert-Habart, 1988).

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