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X-ray investigations of benzopyran derivatives substituted at position 3

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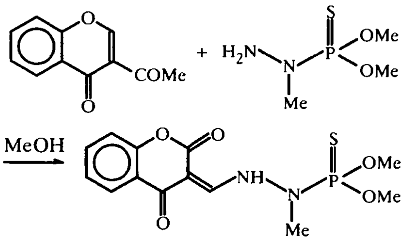
Abstract

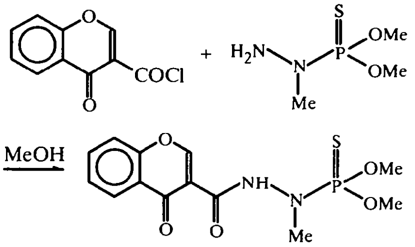
The structures of two isomeric compounds, (*E*)-3-{[2-(dimethoxythiophosphoryl)-2-methylhydrazino]-methylidene}-3,4-dihydro-2*H*-1-benzopyran-2,4-dione, $C_{13}H_{15}N_2O_5PS$, and 3-{[2-(dimethoxythiophosphoryl)-2-methylhydrazino]carbonyl}-3,4-dihydro-4*H*-1-benzopyran-4-one, $C_{13}H_{15}N_2O_5PS$, have been determined from X-ray data and compared. The benzopyran moieties of both molecules are planar. Extra six-membered rings are formed by N—H···O hydrogen bonds. The geometry around the P atoms is tetrahedral, slightly deformed to trigonal pyramidal.

Comment

This paper opens X-ray studies on a group of benzopyran derivatives substituted with phosphorohydrazide at position 3. These compounds are expected to exhibit anticancer activity (Nawrot-Modranka & Graczyk, 1999). Investigations of (*E*)-3-{[2-(dimethoxythiophosphoryl)-2-methylhydrazino]methylidene}-3,4-dihydro-4*H*-1-benzopyran-4-one, (I), were undertaken to determine its tautomeric form in the crystal state, since H^1 NMR spectroscopy did not give conclusive information about its structure. Its isomer, 3-{[2-(dimethoxythiophosphoryl)-2-methylhydrazino]carbonyl}-3,4-dihydro-2*H*-1-benzopyran-2,4-dione, (II), was also studied. The study of (I) and (II) was carried out in order to obtain structural information about the conformation of the rings and the environment around the P atom in both molecules.



(I)



(II)

The title compounds differ from each other only in the position of the carbonyl O atom [O621 in (I) and O51 in (II)]. Their conformations are nearly the same.

The fused benzene and pyran rings are flat and almost coplanar. Both molecules are found with the amino NH group taking part in intramolecular hydrogen bonds, forming planar six-membered rings in both compounds; the maximum deviation from the best plane (Nardelli, 1996) is 0.020 (2) Å for (I) and 0.010 (1) Å for (II).

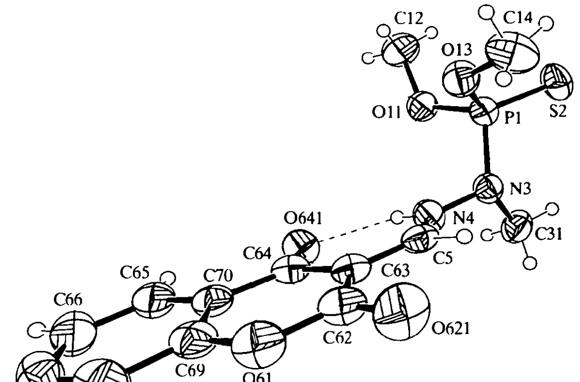


Fig. 1. *ORTEX* (McArdle, 1995) drawing of compound (I), showing the atomic numbering scheme and the intramolecular hydrogen bond. Displacement ellipsoids are shown at the 40% probability level and H atoms are shown as spheres of arbitrary radii.

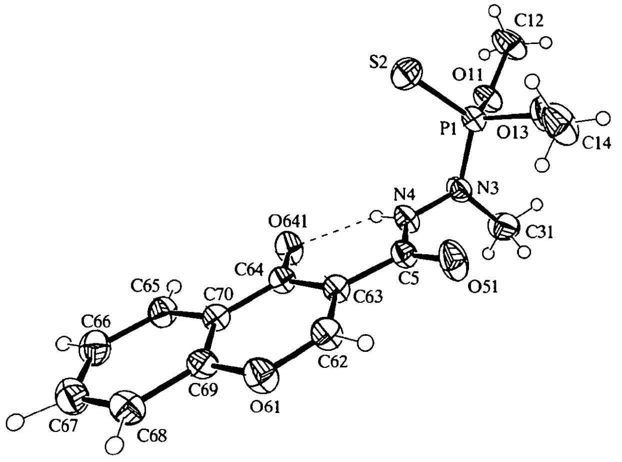


Fig. 2. *ORTEX* (McArdle, 1995) drawing of compound (II), showing the atomic numbering scheme and the intramolecular hydrogen bond. Displacement ellipsoids are shown at the 40% probability level and H atoms are shown as spheres of arbitrary radii.

The planar conformations of the benzopyran skeleton and the hydrogen-bonded rings seem to be stabilized by a weak interaction involving the carbonyl O641 atom and the benzene H651 atom: O···H is 2.57 (3) Å in (I) and 2.53 (2) Å in (II). Also, the weak interaction between O51 and H621 [2.44 (2) Å in (II)] has some influence on the planarity of the molecule.

As expected (Cambridge Structural Database, 1998), the P atoms are tetrahedrally four-coordinate in both molecules. The bond angles around the P atoms (see Tables 1 and 3) indicate a slight deformation towards a trigonal pyramid; this is caused by the different substituents, in particular the relatively long P1—S2 bond.

Bonds distances and angles in both molecules are in good agreement with expected values (Allen *et al.*, 1987).

Experimental

The two title compounds were prepared by the reaction of equimolar quantities of N^1-dimethoxythiophosphoro-N^1-methylhydrazide with methyl 4-oxo-4*H*-1-benzopyran-3-carboxylate [for (I)] or 4-oxo-4*H*-1-benzopyran-3-carbonyl chloride [for (II)] in methanol solutions, as shown in the synthesis scheme above. Suitable crystals were obtained at room temperature by slow evaporation from methanol.

Compound (I)

Crystal data

$C_{13}H_{15}N_2O_5PS$
$M_r = 342.30$
Monoclinic
$P2_1/c$
$a = 10.866$ (2) Å
$b = 12.390$ (1) Å
$c = 11.845$ (1) Å
$\beta = 101.20$ (1)°
$V = 1564.3$ (4) Å^3
$Z = 4$
$D_x = 1.453$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 18.71–22.68°$
$\mu = 0.333$ mm^{-1}
$T = 293$ (2) K
Plate
$0.6 \times 0.5 \times 0.4$ mm
Colourless

Data collection

Rigaku AFC-5*S* diffractometer
$2\theta/\omega$ scan
Absorption correction: analytical (de Meulenaer & Tompa, 1965)
$T_{\min} = 0.831$, $T_{\max} = 0.860$
3800 measured reflections
3617 independent reflections
2135 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.020$
$\theta_{\max} = 27.56°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 16$
$l = -15 \rightarrow 15$
3 standard reflections every 150 reflections intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.110$
$S = 0.943$
3617 reflections
258 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0563P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.039$

$\Delta\rho_{\max} = 0.284$ e Å^{-3}
$\Delta\rho_{\min} = -0.198$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0026 (8)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

P1—O13	1.558 (2)	N3—N4	1.400 (2)
P1—O11	1.577 (2)	N3—C31	1.463 (3)
P1—N3	1.670 (2)	O13—C14	1.431 (3)
P1—S2	1.905 (1)	C5—C63	1.382 (3)
O11—C12	1.446 (3)		
O13—P1—O11	99.9 (1)	N4—N3—C31	112.0 (2)
O13—P1—N3	104.3 (1)	N4—N3—P1	113.7 (1)
O11—P1—N3	102.4 (1)	C31—N3—P1	121.6 (2)
O13—P1—S2	117.7 (1)	C5—N4—N3	121.6 (2)
O11—P1—S2	117.3 (1)	C14—O13—P1	123.4 (2)
N3—P1—S2	113.1 (1)	N4—C5—C63	123.7 (2)
C12—O11—P1	119.6 (2)		

Table 2. *Hydrogen-bonding geometry (Å, °) for (I)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H41···O641	0.81 (3)	1.97 (2)	2.627 (3)	138 (2)

Compound (II)

Crystal data

$C_{13}H_{15}N_2O_5PS$
$M_r = 342.30$
Triclinic
$P\bar{1}$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 24 reflections

$a = 7.666$ (3) Å
$b = 15.521$ (2) Å
$c = 7.470$ (2) Å
$\alpha = 101.53$ (2)°
$\beta = 115.50$ (3)°
$\gamma = 91.91$ (3)°
$V = 778.8$ (4) Å^3
$Z = 2$
$D_x = 1.460$ Mg m^{-3}
D_m not measured

$\theta = 10.86$–15.67°
$\mu = 0.334$ mm^{-1}
$T = 293$ (2) K
Plate
0.7 × 0.6 × 0.3 mm
Colourless

Data collection

Rigaku AFC-5*S* diffractometer
2θ/ω scan
Absorption correction: analytical (de Meulenaer & Tompa, 1965)
$T_{\min} = 0.823$, $T_{\max} = 0.914$
11 308 measured reflections
5654 independent reflections
4593 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.012$
$\theta_{\max} = 32.57$°
$h = -11 \rightarrow 11$
$k = -23 \rightarrow 23$
$l = -11 \rightarrow 11$
3 standard reflections every 150 reflections intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.119$
$S = 1.085$
5654 reflections
261 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0672P)^2 + 0.0863P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.003$

$\Delta\rho_{\max} = 0.514$ e Å^{-3}
$\Delta\rho_{\min} = -0.531$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.093 (7)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Selected geometric parameters (Å, °) for (II)*

P1—O13	1.575 (1)	C63—C5	1.491 (2)
P1—O11	1.570 (1)	N3—N4	1.386 (1)
P1—N3	1.647 (1)	N3—C31	1.446 (2)
P1—S2	1.911 (1)	O51—C5	1.221 (2)
O11—C12	1.438 (2)	C5—N4	1.350 (2)
O13—P1—O11	99.1 (1)	N4—N3—C31	115.7 (1)
O13—P1—N3	99.4 (1)	N4—N3—P1	120.4 (1)
O11—P1—N3	108.2 (1)	C31—N3—P1	122.2 (1)
O13—P1—S2	116.7 (1)	O51—C5—N4	122.9 (1)
O11—P1—S2	116.5 (1)	O51—C5—C63	122.5 (1)
N3—P1—S2	114.6 (1)	N4—C5—C63	114.6 (1)
C12—O11—P1	121.3 (1)	C5—N4—N3	120.7 (1)
C14—O13—P1	121.1 (1)		

Table 4. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H41···O641	0.84 (2)	2.02 (2)	2.684 (1)	135 (2)

For (I), atoms H141, H142 and H143 had U(H) fixed to $1.3U_{\rm eq}$ of their parent atoms. For both (I) and (II), the other methyl H atoms were constrained to their parent C atom by *DFIX* in *SHELXL*97 (Sheldrick, 1997) using a rigid body model. The remaining H atoms had all their parameters refined.

For both 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*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*97; molecular graphics: *ORTEX* (McArdle, 1995). Software used to prepare material for publication: *SHELXL*97 and *PARST* (Nardelli, 1996) for (I); *SHELXL*97 for (II).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1410). Services for accessing these data are described at the back of the journal.

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Dimethyl α-(2-benzyl-1-methyl-4-phenylsulfonylpyrrolo[3,4-*b*]indol-3-yl)maleate

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Abstract

The title molecule, $C_{30}H_{26}N_2O_6S$, consists of a methylpyrrolo[3,4-*b*]indole ring with a phenylsulfonyl, a phenyl and a dimethyl maleate group as exocyclic sub-