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A benzopyran derivative substituted at position 3

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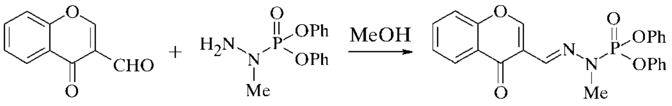
In (*E*)-3-{[(diphenoxyphosphoryl)methylhydrazono]methyl}-4*H*-1-benzopyran-4-one, $C_{23}H_{19}N_2O_5P$, the benzopyran–methylhydrazone moiety is planar and the two phenoxy phenyl rings are inclined at angles of 21.29 (6) and 89.33 (5)°. Weak C—H···O and C—H···N intramolecular interactions exert some influence on the planarity and orientation of that moiety.

Comment

The present paper is part of X-ray studies of a group of benzopyran derivatives substituted with phosphorohydrazide at position 3 (Rybarczyk *et al.*, 1999). These compounds, which are derivatives of biologically active chromones, are of interest because of their expected anticancer activity, by analogy with other chromones (Gabor, 1988; Valenti *et al.*, 1996). The present X-ray investigation of the title benzopyran derivative, (I), was undertaken to obtain structural information regarding the details of the molecular conformation. We were also interested in the weak interactions in the crystal structure.



(I)

The planarity of the pyranoid ring in (I) reveals its aromatic character; the maximum deviation from the least-squares plane (Nardelli, 1996) is 0.016 (2) Å for atom C69. On the other hand, the presence of heteroatom O61 in this cyclic system, as well as the oxo substituent at position 4, significantly modifies the geometric parameters within the ring. The C—C bond distances vary from 1.340 (3) to 1.465 (3) Å, in comparison with a typical aromatic bond length of 1.384 (13) Å (Allen *et al.*, 1987). Moreover, the values of the bond angles within the heterocyclic ring vary from 114.5 (2) to 125.9 (2)° (Table 1).

Fused benzene and pyranoid rings form the benzopyran system, which can be described as planar, with a dihedral angle between the best planes of the rings of 1.21 (6)°.

The hydrazone group (atoms C5, N4 and N3) lies in almost the same plane as the benzopyran moiety; the dihedral angle between the hydrazone and benzopyran least-squares planes is 5.0 (1)°. This coplanar arrangement of the main part of the molecule provides π-conjugation along the C63—C5—N4—N3 bonds and induces planar geometry around atom N3. In addition, the P1—N3 bond length is much closer to the standard $\mathrm{P—N_{planar}}$ distance of 1.65 (2) Å than to the $\mathrm{P—N_{pyramidal}}$ distance of 1.683 (5) Å (Allen *et al.*, 1987).

The $\mathrm{C_{methyl}}$ and P atoms do not deviate much from the hydrazone best plane [0.030 (3) Å for atom C31 and 0.090 (1) Å for atom P1], and they are positioned on opposite sides of the plane. The normal to the hydrazone plane forms an angle of 81.4 (1)° with the P1—O2 bond. As a result, the central P1/N3(C31)/N4/C5/C63 chain of atoms can be regarded as planar.

The geometric parameters around the four-coordinate P atom indicate a slight deformation of the ideal tetrahedron towards a trigonal pyramid, caused by the different substituents and bond types. In particular, the P1═O2 double bond is the shortest and this has an influence on the bond angles in the P environment, which are significantly different from the ideal value of 109.5°.

Even though the majority of the atoms of the molecule lie in nearly the same plane, the tetrahedral geometry of the central phosphonate system results in the overall non-planar molecular conformation. The two phenoxy groups attached to atom P1 are inclined towards the benzopyran–hydrazone moiety; the angles between these rings and the main plane are 21.29 (6)° for the C12–C17 ring and 89.33 (5)° for the C22–C27 ring.

The coplanar arrangement of the main part of the molecule of (I) is additionally stabilized by the availability of acceptors in weak intramolecular contacts, of the non-conventional hydrogen-bonding type, with C—H donors. Some H···O and

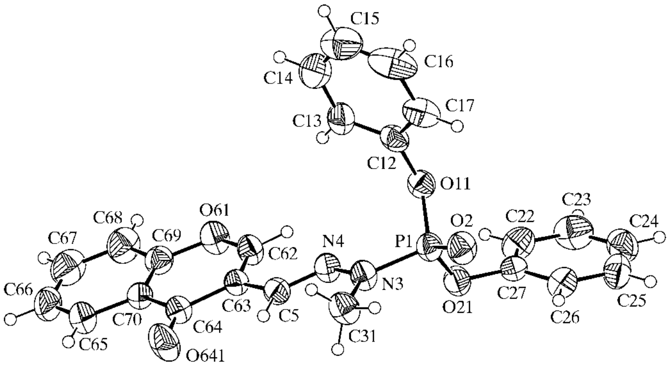


Figure 1
A view of the molecule of (I) showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii.

H···N distances shorter than the sum of the van der Waals radii are observed. The geometry of these weak hydrogen bonds is given in Table 2.

Experimental

Compound (I) was obtained by the reaction of equimolar amounts of 4-oxo-4*H*-benzopyran-3-carboxaldehyde (0.87 g, 0.005 mol) and N^1-diphenyloxyphosphonate-N^1-methylhydrazide (1.38 g) in anhydrous methanol solution (see reaction *Scheme* in *Comment*). After 24 h, the product was precipitated from the reaction solution (m.p. 393–395 K). Crystals of (I) suitable for X-ray analysis were obtained by recrystallization from methanol.

Crystal data

$C_{23}H_{19}N_2O_5P$
$M_r = 434.37$
Monoclinic, $P2_1/n$
$a = 8.312\ (2)$ Å
$b = 10.611\ (1)$ Å
$c = 23.595\ (2)$ Å
$\beta = 90.76\ (1)^\circ$
$V = 2082.8\ (5)$ Å^3
$Z = 4$
$D_x = 1.385$ Mg m^{-3}
$D_m = 1.378$ Mg m^{-3}
D_m measured by flotation in a solution of KI and KBr in water
Mo *Kα* radiation
Cell parameters from 25 reflections
$\theta = 21.3$–23.8°
$\mu = 0.17$ mm^{-1}
$T = 293\ (2)$ K
Prism, colourless
0.6 × 0.5 × 0.4 mm

Table 1
Selected geometric parameters (Å, °).

P1—O2	1.450 (1)	C5—C63	1.460 (3)
P1—O21	1.579 (1)	O61—C62	1.345 (2)
P1—O11	1.588 (1)	O61—C69	1.375 (2)
P1—N3	1.641 (2)	C62—C63	1.340 (3)
N3—N4	1.384 (2)	C64—C70	1.465 (3)
N3—C31	1.455 (3)	C69—C70	1.376 (3)
N4—C5	1.269 (2)		
O2—P1—O21	116.86 (8)	C62—O61—C69	117.9 (2)
O2—P1—O11	115.59 (8)	C63—C62—O61	125.9 (2)
O21—P1—O11	99.66 (7)	C62—C63—C64	119.3 (2)
O2—P1—N3	112.98 (9)	C62—C63—C5	122.0 (2)
O21—P1—N3	103.64 (8)	C64—C63—C5	118.7 (2)
O11—P1—N3	106.52 (8)	O641—C64—C63	122.5 (2)
N4—N3—C31	121.4 (2)	O641—C64—C70	122.9 (2)
N4—N3—P1	115.5 (1)	C63—C64—C70	114.5 (2)
C31—N3—P1	123.1 (2)	O61—C69—C70	121.7 (2)
C5—N4—N3	118.7 (2)	C69—C70—C64	120.7 (2)
N4—C5—C63	120.7 (2)		
O2—P1—N3—N4	170.7 (1)	N3—N4—C5—C63	177.5 (2)
O2—P1—N3—C31	−11.4 (2)	N4—C5—C63—C62	0.0 (3)
C31—N3—N4—C5	−1.4 (3)	N4—C5—C63—C64	−179.4 (2)
P1—N3—N4—C5	176.5 (1)	C5—C63—C64—O641	−4.2 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C31—H312···O2	0.92 (3)	2.50 (3)	3.013 (3)	116 (2)
C5—H51···O641	0.95 (2)	2.49 (2)	2.828 (2)	101 (2)
C65—H65···O641	0.93	2.62	2.873 (3)	96
C62—H62···N4	0.94 (2)	2.62 (2)	2.819 (3)	92 (1)

Data collection

Rigaku AFC-5*S* diffractometer
ω scans
Absorption correction: analytical (de Meulenaer & Tompa, 1965)
$T_{\min} = 0.915$, $T_{\max} = 0.944$
3738 measured reflections
3648 independent reflections
2746 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.015$
$\theta_{\max} = 25^\circ$
$h = -9 \rightarrow 9$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 28$
3 standard reflections every 150 reflections intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.130$
$S = 1.14$
3648 reflections
301 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0798P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.28$ e Å^{-3}
$\Delta\rho_{\min} = -0.24$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.018 (2)

The H atoms of the benzenoid rings were constrained to their parent C atoms by a rigid-body model, using the *AFIX*-43 instruction in *SHELXL*97 (Sheldrick, 1997), with C—H = 0.93 Å. The remaining H atoms were refined freely.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1989); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1989); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1998); software used to prepare material for publication: *SHELXL*97 and *PARST*97 (Nardelli, 1996).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1572). Services for accessing these data are described at the back of the journal.

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