

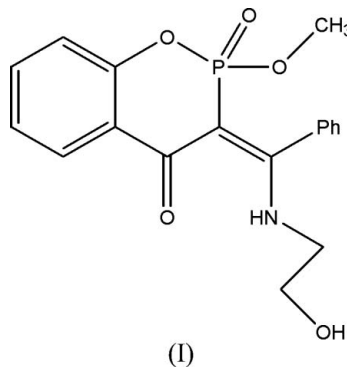
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Elżbieta Budzisz^b^aDepartment of Crystallography and Crystal Chemistry, University of Łódź, Pomorska 149/153, PL-90236 Łódź, Poland, and ^bDepartment of Cosmetic Raw Materials Chemistry, Faculty of Pharmacy, Medical University of Łódź, Muszyńskiego 1, PL-90151 Łódź, Poland

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Key indicators

Single-crystal X-ray study
T = 193 K
Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$
R factor = 0.038
wR factor = 0.102
Data-to-parameter ratio = 13.9For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.3-[α -(2-Hydroxyethylamino)benzylidene]-2-methoxy-2,3-dihydro-1,2 λ^5 -benzoxaphosphinine-2,4-dioneThe title compound, $\text{C}_{18}\text{H}_{18}\text{NO}_5\text{P}$, adopts the keto–amine tautomeric form, forming an intramolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bond. The oxaphosphinine ring has a screw-boat conformation. The molecules are linked by $\text{O}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds and by a π – π stacking interaction.Received 31 August 2006
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Comment

In the search for new therapeutics we have already synthesized several phosphonic analogues of coumarin (Kostka *et al.*, 1998), of interest because of their potential pharmacological activity (Patonay *et al.*, 1984, Roszkopt *et al.*, 1992). We report here on a 1,2-benzoxaphosphinine-2,4-dione derivative as a potential ligand for Pd or Pt complexes with biological activity, in continuation of our structural studies on oxaphosphinin-4-one and chromone derivatives (Budzisz *et al.*, 2001, 2005; Małecka & Budzisz, 2001; Małecka *et al.*, 2004).The heterocyclic ring adopts a screw-boat conformation, with ring-puckering parameters (Cremer & Pople, 1975) $Q_T = 0.425 (1) \text{ \AA}$, $\varphi_2 = 36.7 (3)^\circ$, $\theta_2 = 67.1 (3)^\circ$, and asymmetry parameters (Nardelli, 1983) $\Delta_2(\text{O}2-\text{P}1) = 0.033 (1)$, $\Delta_2(\text{C}3) = 0.073 (1)$. The keto–amine tautomer is favoured over the enol-imine form. Thus there is an intramolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bond that could be classified as a resonance-assisted hydrogen bond (RAHB; Gilli *et al.*, 1994). Such interactions were observed in our previously investigated structures, and also in other coumarin derivatives (Rybarczyk *et al.*, 1999; Rybarczyk-Pirek, Grabowski *et al.*, 2002; Rybarczyk-Pirek, Małecka *et al.*, 2002; Rybarczyk-Pirek *et al.*, 2003).The π -electron delocalization effect characteristic for an RAHB results in a shortening of the formally single bond $\text{C}3-\text{C}4 [1.435 (3) \text{ \AA}]$ and a lengthening of the formally double bond $\text{C}3=\text{C}31 [1.417 (3) \text{ \AA}]$, as well as the elongation of the $\text{C}4=\text{O}4$ bond $[1.250 (2) \text{ \AA}]$ and the shortening of the $\text{C}31-\text{N}32$ bond $[1.320 (3) \text{ \AA}]$. The P atom has a slightly distorted

tetrahedral geometry with an elongated C3–P2 apical bond, but the remaining bond distances and angles are normal (Allen *et al.*, 1987).

The intramolecular N–H···O hydrogen bond generates an envelope five-membered ring, with asymmetry parameter (Nardelli, 1983) $\Delta_s = 0.02$ (1). The ring-puckering parameters (Cremer & Pople, 1975) for the atom sequence C33–C34–O35···H32–N32 are $\theta_2 = 0.70$ (2)° and $\varphi_2 = -2.4$ (2)°. The molecules are linked by three different hydrogen bonds, one of O–H···O type and two of C–H···O type (Table 1). Additionally, the aryl rings (C5–C10) in the molecules at (x, y, z) and $(-x, 2 - y, -z)$ are linked by π – π interactions: the interplanar spacing is 3.429 (2) Å, while the ring-centroid separation is 3.810 (2) Å.

Experimental

3-[1-(2-Hydroxyethylamino)benzylidene]-2-methoxy-2-oxo-2,3-dihydro-2 λ^5 -benzo[e][1,2]oxaphosphinin-4-one was synthesized in the reaction of dimethyl 2-phenyl-4-oxo-4*H*-chromen-3-ylphosphonate (20 mmol) in methanol (10 ml) with ethanolamine (20 mmol) in methanol (5 ml) at room temperature. The precipitated product as a white solid was recrystallized from methanol (Budzisz *et al.*, 2001).

Crystal data

C ₁₈ H ₁₈ NO ₅ P	Z = 8
<i>M_r</i> = 359.30	<i>D_x</i> = 1.440 Mg m ⁻³
Monoclinic, <i>I</i> 2/ <i>a</i>	Mo <i>K</i> α radiation
<i>a</i> = 19.178 (3) Å	μ = 0.20 mm ⁻¹
<i>b</i> = 9.8913 (6) Å	<i>T</i> = 193 (2) K
<i>c</i> = 19.1983 (19) Å	Plate, colourless
β = 114.513 (11)°	0.42 × 0.24 × 0.12 mm
<i>V</i> = 3313.6 (7) Å ³	

Data collection

Stoe IPDS-II diffractometer	16527 measured reflections
φ scans	3166 independent reflections
Absorption correction: multi-scan (<i>XPREP</i> ; Sheldrick, 1996)	2339 reflections with $I > 2\sigma(I)$
<i>T_{min}</i> = 0.946, <i>T_{max}</i> = 0.973	<i>R_{int}</i> = 0.052
	θ_{\max} = 26.0°

Refinement

Refinement on <i>F</i> ²	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.038$	$w = 1/[\sigma^2(F_o^2) + (0.0716P)^2]$
$wR(F^2) = 0.103$	where $P = (F_o^2 + 2F_c^2)/3$
<i>S</i> = 0.95	$(\Delta/\sigma)_{\max} = 0.001$
3166 reflections	$\Delta\rho_{\max} = 0.48 \text{ e } \text{Å}^{-3}$
227 parameters	$\Delta\rho_{\min} = -0.42 \text{ e } \text{Å}^{-3}$

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N32–H32···O4	0.86	1.90	2.581 (2)	135
N32–H32···O5	0.86	2.79	2.864 (2)	86
O35–H35···O21 ⁱ	0.82	1.90	2.717 (2)	173
C5–H5···O4 ⁱⁱ	0.93	2.42	3.287 (3)	155
C314–H314···O35 ⁱⁱⁱ	0.93	2.47	3.365 (3)	160

Symmetry codes: (i) $-x + \frac{1}{2}, -y + \frac{5}{2}, -z + \frac{1}{2}$; (ii) $-x + \frac{1}{2}, y, -z$; (iii) $x, -y + \frac{5}{2}, z + \frac{1}{2}$.

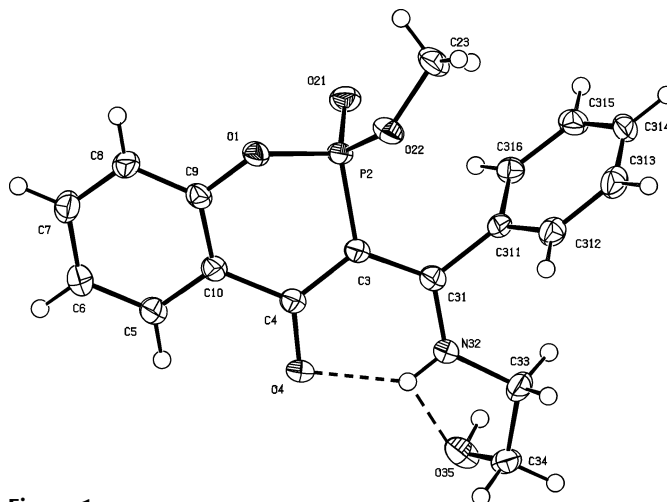


Figure 1

The molecular structure and atomic numbering scheme, showing 50% probability displacement ellipsoids. The intramolecular N–H···O hydrogen bond classified as a resonance-assisted hydrogen bond (RAHB) is shown as a dashed line.

All H atoms were treated as riding atoms with distances C–H = 0.93–0.97 Å, N–H = 0.86 Å and O–H = 0.82 Å, and with $U_{\text{iso}}(\text{H}) = kU_{\text{eq}}(\text{carrier atom})$, where $k = 1.5$ for methyl H and OH, and 1.2 for all other H atoms.

Data collection: *Win-XPOSE* in *IPDS-II Software* (Stoe & Cie, 2000); cell refinement: *Win-CELL* in *IPDS-II Software*; data reduction: *Win-INTEGRATE* in *IPDS-II Software*; program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PARST97* (Nardelli, 1996).

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