

2937 reflections
271 parameters
H atoms constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0746P)^2 + 0.0914P]$
where $P = (F_o^2 + 2F_c^2)/3$

Scattering factors from
*International Tables for
Crystallography* (Vol. C)
Absolute structure: Flack
(1983)
Flack parameter = 0.0 (3)

Table 1. Selected torsion angles ($^\circ$)

C5—C1—C2—C3	-42.8 (2)	C2—C1—C5—C4	31.6 (2)
C1—C2—C3—C4	38.5 (2)	C9—C1—C6—C7	-75.6 (2)
C2—C3—C4—C5	-18.6 (2)	C1—C6—C7—O1	63.7 (2)
C3—C4—C5—C1	-8.7 (2)		

The thermal agitation parameters of the carbonyl O2 atom have important values that could be considered as abnormal. But the carbonyl C16 atom directly connected to O2 is considerably less agitated. So, these large values are the image of an important out-of-plane bending and it is not necessary to introduce atomic sites with fractional occupancy. Atoms O3—O6 of the two nitro groups are also considerably agitated. This seems to be the combined result of rotational movements of these nitro groups around their C—N axes coupled with large translational movements resulting from their terminal position in the molecule. Here also, it is not necessary to introduce atomic sites with fractional occupancy.

Data collection: *CAD-4 EXPRESS* (Enraf-Nonius, 1992). Cell refinement: *CAD-4 EXPRESS*. Data reduction: *NONIUS93* (Baudoux & Evrard, 1993). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997b). Molecular graphics: *PLATON* (Spek, 1990). Software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1180). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.
- Baudoux, G. & Evrard, G. (1993). *NONIUS93. Program for Data Reduction*. Facultés Universitaires Notre-Dame de la Paix, Namur, Belgium.
- Dunitz, J. (1979). *X-ray Analysis And The Structure of Organic Molecules*, p. 429. Ithaca: Cornell University Press.
- Enraf-Nonius (1992). *CAD-4 EXPRESS*. Version 1.1. Enraf-Nonius, Delft, The Netherlands.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Krief, A. & Barbeaux, P. (1987). *J. Chem. Soc. Chem. Commun.* **16**, 1214–1216.
- Krief, A. & Bousbaa, J. (1996). *Synlett*, pp. 1007–1008.
- Luhmer, M., Bartik, K., Dejaegere, A., Bovy, Ph. & Reisse, J. (1994). *Bull. Soc. Chim. Fr.* **131**, 603–606.
- Sheldrick, G. M. (1997a). *SHELXS97. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997b). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Spek, A. L. (1990). *Acta Cryst.* **A46**, C-34.
- Williams, J. H. (1993). *Acc. Chem. Res.* **26**, 593–598.

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2-Methoxy-3-methyl-6-[(triphenylphosphoranylidene)amino]pyrimidin-4(3H)-one and 3-Methyl-2-methylthio-6-[(triphenylphosphoranylidene)amino]pyrimidin-4(3H)-one

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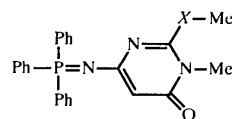
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Abstract

Structure analyses of the 2-methoxy- [C₂₄H₂₂N₃O₂P, (1)] and 2-methylthio- [C₂₄H₂₂N₃OPS, (2)] title compounds show that while they are not isomorphous, they do have very similar conformations in the solid state. In both compounds, there are deviations from ideal tetrahedral symmetry around the P atoms, *e.g.* the N—P—C angles are in the range 105.57 (9)–117.81 (9) $^\circ$ in (1) and 105.75 (12)–118.22 (13) $^\circ$ in (2). This is consistent with the behaviour of the methyl-group signals in their NMR spectra.

Comment

The title compounds, (1) and (2), and related compounds have been used as intermediates in several reactions in which the triphenylphosphoranylidene group is used to protect an amino group from unwanted reactions (Wamhoff & Schupp, 1986; Wamhoff *et al.*, 1986). The X-ray analyses of (1) and (2) were undertaken to establish the solid-state conformations and correlate these with NMR spectral data.



- (1) X = O
(2) X = S

Views of (1) and (2) are presented in Figs. 1 and 2, respectively; the compounds are not isomorphous, but they are isostructural. The methoxy group in (1) and the

methylthio group in (2) are spatially arranged with the methyl C2A atom directed towards the electron cloud of the C11–C16 aromatic ring. The distance of C2A from the mean plane of this ring is 3.759 (3) Å in (1) and 3.477 (4) Å in (2). In addition, the N6–P6–C11 angle [117.81 (9)° in (1) and 118.22 (13)° in (2)] is the largest of the tetrahedral angles around the P atom in each molecule. This spatial disposition explains the behaviour of the respective methyl groups of (1) and (2) in ¹H NMR, because they are shielded by the ring-current effect. Thus, the signals corresponding to the protons of these groups are down-shifted [δ OCH₃ (CDCl₃) = 3.22 p.p.m. for (1) and δ SCH₃ (CDCl₃) = 1.55 p.p.m. for (2)] with respect to those of their precursor compounds [δ OCH₃ (DMSO-*d*₆) = 3.88 p.p.m. for the precursor of (1) and δ SCH₃ (DMSO-*d*₆) = 2.40 p.p.m. for the precursor of (2)].

The pyrimidine dimensions in the two compounds show no significant geometrical differences greater than

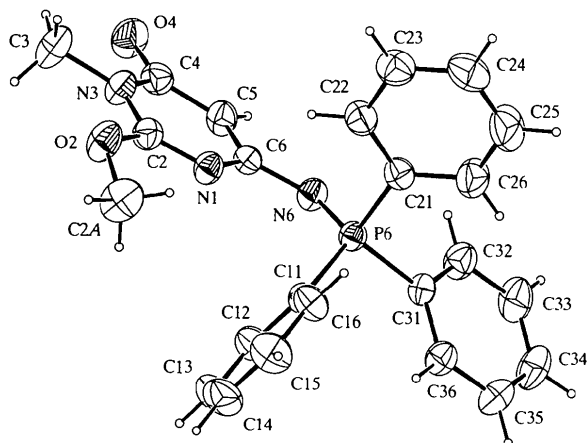


Fig. 1. A view of (1) with the numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

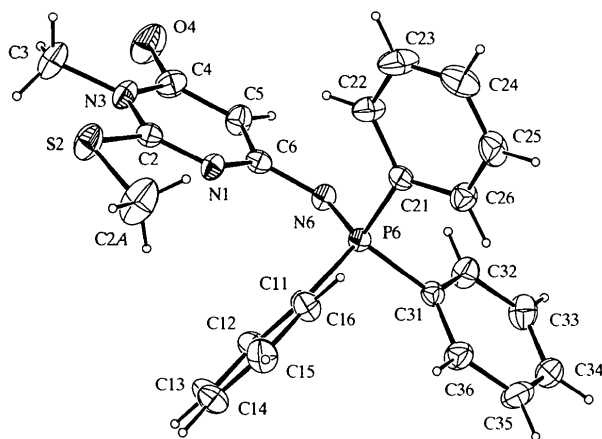


Fig. 2. A view of (2) with the numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

3 σ and are similar to the geometries found in the structures of the 4-amino-2-methoxy- and 4-amino-2-methylthio compounds (Low *et al.*, 1994). The N–P bonds in the two compounds [1.592 (2) Å in (1) and 1.588 (2) Å in (2)] are identical within experimental error. The P–C bonds are in the range 1.798 (2)–1.811 (2) Å in (1) and 1.796 (3)–1.808 (3) Å in (2), with the N–P–C angles in the range 105.57 (9)–117.81 (9)° in (1) and 105.75 (12)–118.22 (13)° in (2). There are no unusual intermolecular contacts and examination of the structures with PLATON (Spek, 1998) shows that there are no voids in the crystal lattices.

Experimental

The title compounds were prepared from 6-amino-2-methoxy-3-methylpyrimidin-4(3*H*)-one [for (1)] and from 6-amino-3-methyl-2-methylthiopyrimidin-4(3*H*)-one [for (2)] by the method used for the preparation of 1,3-dimethyl-6-[(triphenylphosphoranylidene)amino]pyrimidin-4(3*H*)-one described by Wamhoff & Schupp (1986) and Wamhoff *et al.* (1986). Both compounds were crystallized from ethanol.

Compound (1)

Crystal data

C₂₄H₂₂N₃O₂P

M_r = 415.42

Monoclinic

*I*2/a

a = 16.599 (2) Å

b = 13.957 (2) Å

c = 18.105 (3) Å

β = 95.929 (12)°

V = 4172.0 (10) Å³

Z = 8

D_x = 1.323 Mg m⁻³

D_m not measured

Mo K α radiation

λ = 0.7107 Å

Cell parameters from 25 reflections

θ = 10.2–17.5°

μ = 0.158 mm⁻¹

T = 294 (1) K

Block

0.41 × 0.28 × 0.26 mm

Colourless

Data collection

Enraf–Nonius CAD-4

diffractometer

$\theta/2\theta$ scans

Absorption correction: none

4693 measured reflections

4543 independent reflections

2432 reflections with

I > 2 σ (*I*)

R_{int} = 0.011

θ_{\max} = 26.90°

h = –21 → 21

k = 0 → 17

l = 0 → 23

3 standard reflections

frequency: 120 min

intensity variation: 2.1%

Refinement

Refinement on *F*²

R[*F*² > 2 σ (*F*²)] = 0.039

wR(*F*²) = 0.113

S = 0.964

4543 reflections

273 parameters

H atoms riding

w = 1/[$\sigma^2(F_o^2) + (0.0626P)^2$]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} < 0.001

$\Delta\rho_{\max}$ = 0.352 e Å⁻³

$\Delta\rho_{\min}$ = –0.289 e Å⁻³

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

Compound (2)*Crystal data*C₂₄H₂₂N₃O₃*M_r* = 431.48

Triclinic

P $\bar{1}$ *a* = 8.666 (2) Å*b* = 10.985 (3) Å*c* = 12.373 (3) Å α = 79.291 (12)° β = 75.62 (2)° γ = 70.693 (14)°*V* = 1069.8 (4) Å³*Z* = 2*D_x* = 1.339 Mg m⁻³*D_m* not measuredMo *K* α radiation λ = 0.7107 Å

Cell parameters from 250 reflections

 θ = 1.97–25.04° μ = 0.247 mm⁻¹*T* = 150 (1) K

Block

0.30 × 0.28 × 0.26 mm

Yellow

Data collection

Enraf–Nonius diffractometer with FAST area detector

MADNES scans (Pflugrath & Messerschmidt, 1989)

Absorption correction: none

4077 measured reflections

2788 independent reflections

2507 reflections with

I > 2σ(*I*)*R*_{int} = 0.073 θ _{max} = 25.04°*h* = -9 → 9*k* = -12 → 11*l* = -14 → 13*Refinement*Refinement on *F*²*R* [*F*² > 2σ(*F*²)] = 0.065*wR* (*F*²) = 0.164*S* = 1.084

2788 reflections

273 parameters

H atoms riding

w = 1/[σ²(*F*_o²) + (0.1220*P*)²]where *P* = (*F*_o² + 2*F*_c²)/3(Δ/σ)_{max} = 0.001Δρ_{max} = 0.778 e Å⁻³Δρ_{min} = -0.474 e Å⁻³

Extinction correction: none

Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

	(1)	(2)
N6—C6	1.360 (2)	1.348 (3)
P6—N6	1.592 (2)	1.588 (2)
P6—C11	1.799 (2)	1.808 (3)
P6—C21	1.811 (2)	1.803 (3)
P6—C31	1.798 (2)	1.796 (3)
P6—N6—C6	125.77 (14)	127.7 (2)
N6—P6—C11	117.81 (9)	118.22 (13)
N6—P6—C21	113.53 (9)	112.87 (13)
N6—P6—C31	105.57 (9)	105.75 (12)
C11—P6—C21	107.00 (9)	105.58 (12)
C11—P6—C31	106.53 (9)	107.03 (13)
C21—P6—C31	105.50 (9)	106.76 (13)
N1—C2—O2—C2A	-12.4 (3)	-
N1—C2—S2—C2A	-	-3.2 (3)
C6—N6—P6—C11	46.9 (2)	45.7 (3)

Molecule (1) crystallized in the monoclinic system; space groups *I2/a* or *la* were indicated by the systematic absences, and *I2/a* was assumed and confirmed by the analysis. Molecule (2) crystallized in the triclinic system; space group *P* $\bar{1}$ was assumed and confirmed by the analysis. In both structures, H atoms were treated as riding atoms, with C—H 0.93–0.98 Å and N—H 0.86 Å. Examination of the structures with *PLATON* (Spek, 1998) showed that there were no solvent-accessible voids in the crystal lattices

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1992) for (1); *MADNES* (Pflugrath & Messerschmidt, 1989) for (2). Cell refinement: *SET4* and *CELDIM* in *CAD-4-PC Software* for (1); *MADNES* for (2). Data reduction: *NRCVAX94* (Gabe *et al.*, 1989) for (1); *MADNES* and *NRCVAX94* for (2). For both compounds, program(s) used to solve structures: *NRCVAX94*; program(s) used to refine structures: *NRCVAX94* and *SHELXL93* (Sheldrick, 1993); molecular graphics: *NRCVAX94* and *PLATON*; software used to prepare material for publication: *NRCVAX94* and *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1053). Services for accessing these data are described at the back of the journal.

References

- Enraf–Nonius (1992). *CAD-4-PC Software*. Version 1.1. Enraf–Nonius, Delft, The Netherlands
- Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
- Low, J. N., Scrimgeour, S. N., Egglisshaw, C., Howie, R. A., Moreno-Carretero, M. N. & Hueso-Urena, F. (1994). *Acta Cryst.* **C50**, 1329–1333.
- Pflugrath, J. W. & Messerschmidt, A. (1989). *MADNES*. Version II. Delft Instruments, The Netherlands.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Spek, A. L. (1998). *PLATON. Molecular Geometry and Graphics Program*. Version of January 1998. University of Utrecht, The Netherlands.
- Wamhoff, H. & Schupp, W. (1986). *J. Org. Chem.* **51**, 2787–2789.
- Wamhoff, H., Schupp, W., Kirfel, A. & Will, G. (1986). *J. Org. Chem.* **51**, 149–154.

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'Guest-Free' Dianin's Compound

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Abstract

The existence of empty hour-glass-shaped cavities is confirmed for the crystal of the title compound, 4-(*p*-hydroxyphenyl)-2,2,4-trimethylchroman [systematic name: