

***O,O*-Diphenyl 2-methyl-1-(3-phenylthioureido)-propanephosphonate**

Lilianna Chęcińska,<sup>a\*</sup> Magdalena Małecka,<sup>a</sup> Tomasz A. Olszak<sup>a</sup> and Zbigniew H. Kudzin<sup>b</sup>

<sup>a</sup>Department of Crystallography, University of Łódź, Pomorska 149/153, PL-90236 Łódź, Poland, and <sup>b</sup>Department of Organic Chemistry, University of Łódź, Narutowicza 68, PL-90136 Łódź, Poland

Correspondence e-mail: lilach@krysia.uni.lodz.pl

**Key indicators**

Single-crystal X-ray study

*T* = 293 K

Mean  $\sigma$ (C–C) = 0.005 Å

*R* factor = 0.054

w*R* factor = 0.141

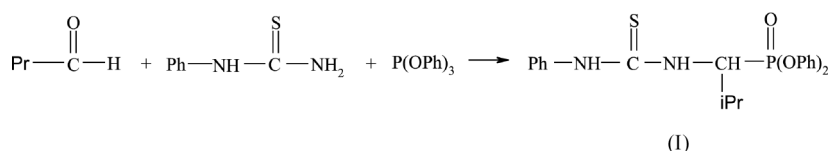
Data-to-parameter ratio = 14.7

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The crystal structure of the title compound, C<sub>23</sub>H<sub>25</sub>N<sub>2</sub>O<sub>3</sub>PS, is reported. The centrosymmetrically related molecules are connected by N–H···O hydrogen bonds and, as a result, the molecules exist as dimers. The geometry about the P atom can be described as distorted tetrahedral.

**Comment**

*O,O*-Diphenyl *N*-phenylthioureidoalkanephosphonates are synthetically attractive due to their broad applications in the synthesis of various 1-aminoalkanephosphonic acids (Kudzin & Stec, 1978; Kudzin, 1996; Kafarski & Zoń, 2000). Moreover, this class of phosphonates presents a structural analogy to PTC-amino acids (phenylthiocarbamoylamino acids). There are no reported crystal structure determinations of phosphonylated thioureas, so this prompted us to perform X-ray investigations on this series of compounds. The study was carried out in order to obtain structural information about the geometry around the P atom and was also directed to the assignment of types and locations of molecular hydrogen bonds.



The title compound, (I), contains the *N*-phenylthioureide group, *O,O*-diphenylphosphonate moiety and isopropyl group linked by means of the methine carbon (C2).

The geometry around the P atom is distorted tetrahedral, the angles varying from 116.3 (1) to 101.5 (1)°. All angles involving the non-ester O atom are larger than the others.

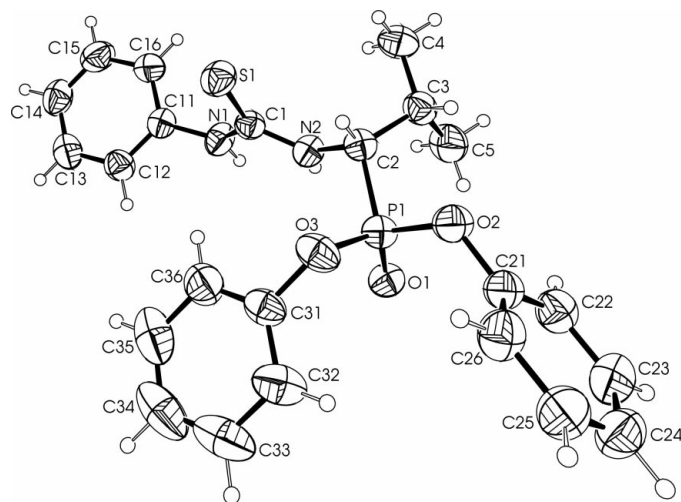
In the present structure, atom O1 participates in two N–H···O hydrogen bonds. The interaction involving atoms N1, H1 and O1<sup>i</sup> [symmetry code: (i)  $-x+2, -y+1, -z+1$ ] creates a pattern whose first-level graph-set descriptor (Bernstein *et al.*, 1995) is  $R_2^2(14)$ . Moreover, interaction N2–H2···O1<sup>i</sup> produces an  $R_2^2(10)$  motif. The combination of two hydrogen bonds provides a finite pattern of type  $R_2^1(6)$ . Furthermore, this second level hydrogen-bonding motif seems to have an influence in shortening the H1···H2 distance [1.95 (4) Å], as both atoms are connected to the same acceptor-O atom. Finally, the molecules exist as dimers.

The benzene rings are planar within experimental error. The thioureide group is also flat, as expected. The S1–C1 bond length, 1.663 (2) Å, is shorter than the unweighted mean value, 1.681 Å, given for C=S in thioureas (Allen *et al.*, 1987),

Received 7 November 2001

Accepted 15 November 2001

Online 24 November 2001



**Figure 1**  
The structure of the title compound with the atom-labeling scheme. Displacement ellipsoids are drawn at the 40% probability level.

but longer than 1.658 (2) Å (Zhang *et al.*, 1996) and 1.659 (3) Å (Cao *et al.*, 1996) for thioureas. The decrease in the C1=S1 bond length is reflected in the elongation of the N—Csp<sup>2</sup> distances (N1—C1 and N2—C1) compared with the mean value of 1.346 Å (Allen *et al.*, 1987). The dihedral angle between the mean plane of the phenyl ring C11—C16 and the thiourea moiety is 70.3 (1)°.

## Experimental

*N*-Phenylthiourea diphosphonate was prepared by condensation of the appropriate aldehyde, *N*-phenylthiourea and triphenyl phosphite (Kudzin & Stec, 1978). The resulting compound was purified by crystallization from a chloroform/ethanol solvent system. The purity was checked by means of <sup>31</sup>P NMR, <sup>1</sup>H NMR and TLC analysis.

### Crystal data

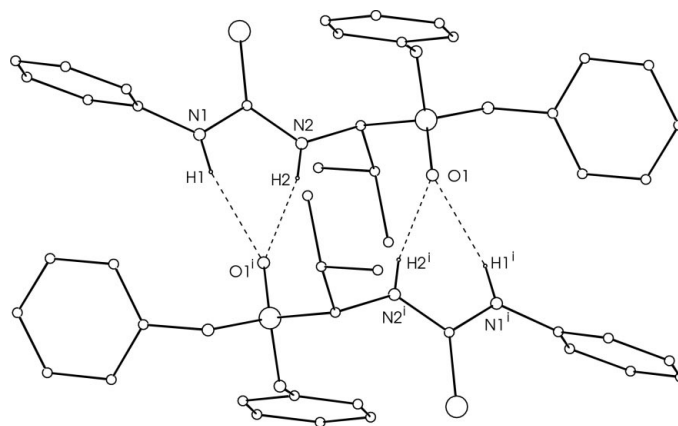
C<sub>23</sub>H<sub>25</sub>N<sub>2</sub>O<sub>3</sub>PS  
*M<sub>r</sub>* = 440.48  
 Monoclinic, *P*<sub>2</sub><sub>1</sub>/*n*  
*a* = 10.061 (1) Å  
*b* = 20.561 (1) Å  
*c* = 11.375 (1) Å  
 $\beta$  = 105.38 (1)°  
*V* = 2268.8 (3) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.290 Mg m<sup>-3</sup>  
*D<sub>m</sub>* = 1.289 Mg m<sup>-3</sup>

*D<sub>m</sub>* measured by flotation in xylene, bromobenzene, heptane and toluene  
 Cu *K*α radiation  
 Cell parameters from 25 reflections  
 $\theta$  = 22.5–30.3°  
 $\mu$  = 2.15 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Plate, colorless  
 0.45 × 0.40 × 0.20 mm

### Data collection

Rigaku AFC-5S diffractometer  
 $\omega$  scans  
 Absorption correction: analytical (de Meulenaer & Tompa, 1965)  
*T<sub>min</sub>* = 0.405, *T<sub>max</sub>* = 0.671  
 4505 measured reflections  
 4266 independent reflections  
 3042 reflections with *I* > 2σ(*I*)

*R<sub>int</sub>* = 0.066  
 $\theta_{\max}$  = 72.6°  
*h* = 0 → 12  
*k* = 0 → 24  
*l* = -14 → 13  
 3 standard reflections every 150 reflections  
 intensity decay: <2%



**Figure 2**  
A view of the dimeric molecules [symmetry code: (i)  $-x+2, -y+1, -z+1$ ]. All H atoms, except H1 and H2 and their symmetry equivalents, have been omitted for clarity.

### Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.054  
*wR* (*F*<sup>2</sup>) = 0.141  
*S* = 0.92  
 4266 reflections  
 291 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0998P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.43 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.42 \text{ e \AA}^{-3}$   
 Extinction correction: *SHELXL97*  
 Extinction coefficient: 0.0159 (8)

**Table 1**

Selected geometric parameters (Å, °).

S1—C1	1.663 (2)	C3—C4	1.518 (4)
C1—N1	1.352 (3)	C3—C5	1.521 (4)
C1—N2	1.357 (3)	P1—O1	1.4696 (15)
N1—C11	1.425 (3)	P1—O3	1.5656 (17)
N2—C2	1.451 (3)	P1—O2	1.5791 (16)
C2—C3	1.540 (3)	O3—C31	1.413 (3)
C2—P1	1.803 (2)	O2—C21	1.413 (3)
N1—C1—N2	112.3 (2)	C4—C3—C2	109.9 (2)
N1—C1—S1	123.75 (18)	C5—C3—C2	113.7 (2)
N2—C1—S1	123.90 (17)	O1—P1—O3	113.74 (10)
C1—N1—C11	126.1 (2)	O1—P1—O2	115.01 (9)
C1—N2—C2	125.2 (2)	O3—P1—O2	103.40 (10)
N2—C2—C3	113.0 (2)	O1—P1—C2	116.26 (10)
N2—C2—P1	106.62 (16)	O3—P1—C2	105.32 (11)
C3—C2—P1	115.19 (17)	O2—P1—C2	101.53 (10)
C4—C3—C5	110.9 (2)		

**Table 2**

Hydrogen-bonding 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>
N1—H1...O1 <sup>i</sup>	0.85 (3)	2.16 (3)	2.975 (3)	162 (3)
N2—H2...O1 <sup>i</sup>	0.78 (3)	2.17 (3)	2.932 (3)	165 (3)

Symmetry code: (i) 2 - *x*, 1 - *y*, 1 - *z*.

All H atoms of methyl and phenyl groups were geometrically placed. All methyl-H atoms were constrained to their parent atoms as

a rigid body ( $C-H = 0.96 \text{ \AA}$ ) and the  $U_{iso}$  values were refined as equal to  $1.5U_{eq}$  of their C parent atoms. All phenyl-H atoms were constrained to their parent atoms as a rigid body ( $C-H = 0.93 \text{ \AA}$ ) and the  $U_{iso}$  values were refined as equal to  $1.2U_{eq}$  of their parent C atoms. All other H atoms (H1, H2, H201 and H301) were located in a difference map and refined isotropically.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1989a); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1989b); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEX* (McArdle, 1995) and *PLUTON92* (Spek, 1992); software used to prepare material for publication: *PARST97* (Nardelli, 1996).

We thank Professor Dr Hab. M. Bukowska-Strzyżewska for helpful advice. Financial support from the University of Łódź (grant No. 505/667) is gratefully acknowledged.

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