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O,O-Diphenyl 1-(3-phenylthioureido)ethanephosphonate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.051
wR factor = 0.130
Data-to-parameter ratio = 15.0

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

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The crystal structure of the title compound, $C_{21}H_{21}N_2O_3PS$, is reported. In the structure, centrosymmetrically related molecules are linked by N—H···O hydrogen bonds and form dimers. The geometry around the P atom indicates a distorted tetrahedron.

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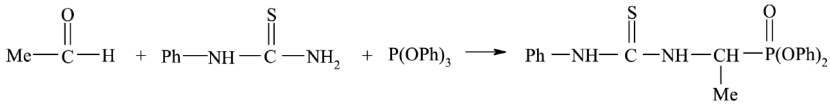
Comment

O,O-Diphenyl *N*-phenylthioureidoalkanephosphonates, the only reported class of phosphonylated thioureas, exhibit close structural analogy to PTC-amino acids (phenylthiocarbamoylamino acids) and therefore are considered as compounds of potential biological activity. Moreover, this class of phosphonates is also synthetically attractive due to their broad applications in the synthesis of phosphonic analogs of natural amino acids (Kudzin & Stec, 1978; Kudzin, 1996; Kafarski & Zoń, 2000).



(I)

The presence of two different NH units in the thioureido fragment and also the phosphonyl moiety, creates a possibility of a variety of hydrogen-bond interactions, indicated previously by the IR spectra of PTC-derivatives of a series of *S*-alkylphosphonocysteines (Kudzin, 1981).

For these reasons, the structural analysis of *O,O*-diphenyl *N*-phenylthioureidoalkanephosphonate, (I), presents an interesting goal for crystallographic investigations, in particular, directed to the assignment of types and locations of molecular hydrogen bonds.

The S atom does not act as an acceptor of hydrogen bonds as it does in other structures including the thiourea moiety (Ramnathan *et al.*, 1996; Steiner, 1998; Shanmuga Sundara Raj *et al.*, 1999; West *et al.*, 1999). In the present structure, atom O1 is the only acceptor and is involved in two N—H···O hydrogen bonds. Atom N1 acts as a donor to $O1^{i}$ [symmetry code: (i) $-x+1$, $-y+1$, $-z+1$] generating an $R_2^2(14)$ motif (Bernstein *et al.*, 1995). Moreover, the N2—H2···$O1^{i}$ interaction 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 form dimers.

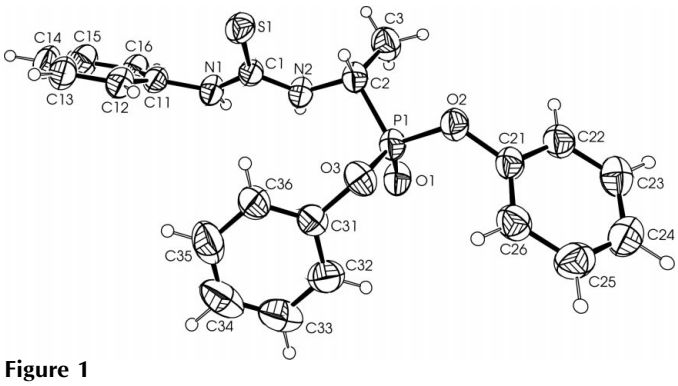


Figure 1
The structure of the title compound with the atom-labeling scheme. Displacement ellipsoids are drawn at the 40% probability level.

The bonds and angles around the P atom indicate a distortion of the tetrahedron caused by different substituents and bond types, *viz*. the double P1═O1 bond and single P1—C2 bond.

The benzene rings are planar within experimental error. The thioureide group is also flat, as expected. The S1—C1 bond length, 1.671 (2) Å, is close to the unweighted mean value of 1.681 Å for the C═S distance in thioureas (Allen *et al.*, 1987). The N—Csp^2 distances (N1—C1 and N2—C1) are in good agreement with the mean value of 1.346 Å in the above reference. The dihedral angle between the mean plane of the phenyl ring C11–C16 and the thiourea moiety is 43.7 (1)°. The relevant torsion angles describing the orientations are S1—C1—N1—C11 = −1.8 (4)° and C1—N1—C11—C12 = −44.5 (4)°.

Experimental

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

Crystal data

$C_{21}H_{21}N_2O_3PS$
M_r = 412.43
Triclinic, $P\overline{1}$
a = 9.753 (1) Å
b = 10.069 (1) Å
c = 12.255 (1) Å
α = 98.17 (1)°
β = 103.37 (1)°
γ = 111.63 (1)°
V = 1053.5 (2) Å^3
Z = 2
D_x = 1.300 Mg m^{-3}
D_m = 1.294 Mg m^{-3}
D_m measured by flotation in xylene, bromobenzene, heptane & toluene
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 22.5–30.4°
μ = 2.28 mm^{-1}
T = 293 (2) K
Prism, colorless
0.5 × 0.3 × 0.3 mm

Data collection

Rigaku AFC-5*S* diffractometer
ω scans
Absorption correction: analytical (de Meulenaer & Tompa, 1965)
T_{min} = 0.356, T_{max} = 0.619
4248 measured reflections
3996 independent reflections
2609 reflections with $I > 2\sigma(I)$
R_{int} = 0.014
θ_{max} = 72.6°
$h = -12 \rightarrow 11$
$k = 0 \rightarrow 12$
$l = -15 \rightarrow 15$
3 standard reflections every 150 reflections intensity decay: <2%

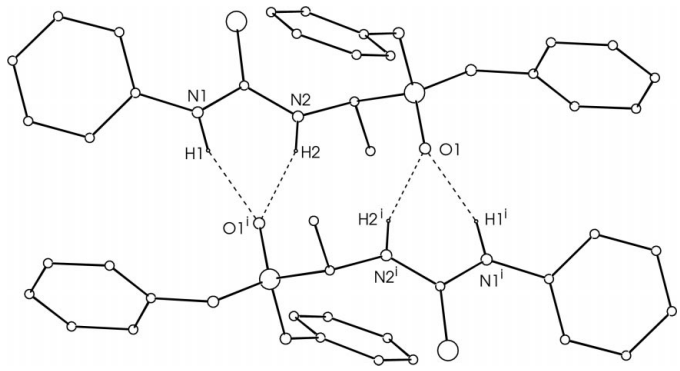


Figure 2
A view of the dimeric molecules [symmetry code: (i) $-x+1, -y+1, -z+1$]. All H atoms, except H1 and H2 and their symmetry equivalents, have been omitted for clarity.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.130
S = 1.04
3995 reflections
267 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0837P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.51 e Å^{-3}
Extinction correction: *SHELXL*
Extinction coefficient: 0.0125 (10)

Table 1
Selected geometric parameters (Å, °).

S1—C1	1.671 (2)	C2—P1	1.805 (3)
C1—N2	1.347 (3)	P1—O1	1.465 (2)
C1—N1	1.355 (3)	P1—O2	1.566 (2)
N1—C11	1.416 (3)	P1—O3	1.574 (2)
N2—C2	1.451 (3)	O2—C21	1.423 (3)
C2—C3	1.517 (4)	O3—C31	1.410 (3)
N2—C1—N1	112.3 (2)	C3—C2—P1	111.9 (2)
N2—C1—S1	123.0 (2)	O1—P1—O2	115.69 (10)
N1—C1—S1	124.7 (2)	O1—P1—O3	114.08 (11)
C1—N1—C11	128.9 (2)	O2—P1—O3	102.22 (10)
C1—N2—C2	124.8 (2)	O1—P1—C2	113.74 (12)
N2—C2—C3	111.6 (2)	O2—P1—C2	102.43 (11)
N2—C2—P1	106.6 (2)	O3—P1—C2	107.37 (11)
S1—C1—N1—C11	−1.8 (4)	C1—N1—C11—C12	−44.5 (4)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1^{i}	0.90 (3)	2.03 (3)	2.896 (3)	161 (3)
N2—H2···O1^{i}	0.85 (3)	2.08 (3)	2.897 (3)	160 (3)

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

All H atoms of the methyl and phenyl groups were geometrically placed. All methyl-H atoms were constrained to their parent atom as a rigid body (C—H = 0.96 Å) and the U_{iso} values were refined as equal to $1.5U_{eq}$ of their C parent atom. All phenyl-H atoms were constrained to their parent atoms as a rigid body (C—H = 0.93 Å) and the U_{iso} values were refined as equal to $1.2U_{eq}$ of their parent C

atoms. All other H atoms (H1, H2 and H201) were located in a difference map and refined isotropically.

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 structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEX* (McArdle, 1995) and *PLUTON*92 (Spek, 1992); software used to prepare material for publication: *PARST*97 (Nardelli, 1996).

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