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Structural studies of (*N*-phenylthioureidoalkyl- and -aryl)phosphonates

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The crystal structures of three (*N*-phenylthioureidoalkyl- and -aryl)phosphonates, *i.e.* diphenyl [(3-phenylthioureido)phenylpropyl]phosphonate, diphenyl [1-(3-phenylthioureido)benzyl]phosphonate and diphenyl [2,2-dimethyl-1-(3-phenylthioureido)propyl]phosphonate, have been determined by X-ray diffraction. The conformations of the title molecules, the geometry of the thioureide fragments and molecular packing arrangements are analyzed and compared with literature data.

1. Introduction

(*N*-Phenylthioureidoalkyl- and -aryl)phosphonates have attracted considerable interest because of their applications as herbicides and as flame retardants in the production of cotton textiles (Birum, 1976, 1977*a*,*b*). Here we report the crystal structures for the following derivatives:

(I) diphenyl [(3-phenylthioureido)phenylpropyl]phosphonate,

(II) diphenyl [1-(3-phenylthioureido)benzyl]phosphonate and

(III) diphenyl [2,2-dimethyl-1-(3-phenylthioureido)propyl]phosphonate.

The molecules of these three compounds are differentiated by the substituent at the methine C atom: phenylethyl (I), phenyl (II) and *tert*-butyl (III), respectively; see Scheme 1.

The aim of our study is not only to present new structural data but also to compare the title crystals with previously published derivatives (Chęcińska *et al.*, 2001*a*,*b*; Chęcińska, Sieroń *et al.*, 2003; Chęcińska, Grabowski & Małecka, 2003). This analysis presents an opportunity to investigate the effect of various substituents on the molecular geometry and on the crystal packing of (*N*-phenylthioureidoalkyl- and -aryl)phosphonates.

2. Experimental

2.1. Syntheses

(*N*-Phenylthioureidoalkyl- and -aryl)phosphonates (I)–(III) were synthesized according to the modified thioureidoalkylphosphonate procedure (Kudzin & Stec, 1978). Aldehydes (trimethylacetaldehyde, benzaldehyde, phenylacetaldehyde and 3-phenylpropionaldehyde), *N*-phenylthiourea and triphenyl phosphite were purchased from Aldrich and were not purified before use.

N-Phenylthiourea (2 mmol, 310 mg) and aldehyde (2.2 mmol) were dissolved, with stirring, at 323–333 K (oil bath) in glacial acetic acid (5 ml). To this solution triphenyl

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Table 1
Crystallographic data, data collection and refinement for (I), (II) and (III).

	I	II	III
Crystal data			
Chemical formula	$C_{28}H_{27}N_2O_3PS$	$C_{26}H_{23}N_2O_3PS$	$C_{24}H_{27}N_2O_3PS$
M_r	502.55	474.49	454.51
Cell setting, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$
a, b, c (Å)	9.951 (1), 12.201 (1), 11.844 (1)	9.953 (1), 10.046 (1), 12.701 (1)	10.688 (3), 9.888 (2), 22.961 (2)
α, β, γ (°)	100.40 (1), 102.90 (1), 102.90 (1)	96.66 (1), 104.45 (1), 99.84 (1)	90.00, 97.790 (1), 90.00
V (Å^3)	1325.6 (2)	1194.8 (2)	2404.2 (9)
Z	2	2	4
D_x (Mg m^{-3})	1.259	1.319	1.256
Radiation type	Cu $K\alpha$	Cu $K\alpha$	Cu $K\alpha$
No. of reflections for cell parameters	25	22	25
θ range (°)	38.2–39.9	22.6–29.5	22.7–28.8
μ (mm^{-1})	1.91	2.09	2.04
Temperature (K)	293 (2)	293 (2)	293 (2)
Crystal form, colour	Prism, colourless	Plate, colourless	Prism, colourless
Crystal size (mm)	0.50 × 0.30 × 0.20	0.2 × 0.2 × 0.1	0.5 × 0.5 × 0.45
Data collection			
Diffractometer	AFC5S Rigaku	AFC5S Rigaku	AFC5S Rigaku
Data collection method	ω scans	ω scans	ω scans
Absorption correction	Analytical	Analytical	Analytical
$T_{\min}$	0.448	0.675	0.427
$T_{\max}$	0.701	0.836	0.464
No. of measured, independent and observed reflections	4878, 4637, 3089	4431, 4169, 2147	4439, 4193, 3100
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
$R_{\rm int}$	0.030	0.019	0.015
$\theta_{\max}$ (°)	67.5	67.5	67.5
Range of h, k, l	$-11 \Rightarrow h \Rightarrow 11$	$-11 \Rightarrow h \Rightarrow 11$	$-12 \Rightarrow h \Rightarrow 12$
	$-14 \Rightarrow k \Rightarrow 14$	$-11 \Rightarrow k \Rightarrow 12$	$-8 \Rightarrow k \Rightarrow 11$
	$-11 \Rightarrow l \Rightarrow 14$	$-15 \Rightarrow l \Rightarrow 15$	$-27 \Rightarrow l \Rightarrow 27$
No. and frequency of standard reflections	3 every 150 reflections	3 every 150 reflections	3 every 150 reflections
Intensity decay (%)	<2	<2	<2
Refinement			
Refinement on	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.041, 0.119, 0.94	0.038, 0.090, 1.00	0.045, 0.137, 1.06
No. of reflections	4637	4169	4193
No. of parameters	325	307	289
H-atom treatment	Mixture of independent and constrained refinement	Mixture of independent and constrained refinement	Mixture of independent and constrained refinement
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0663P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$[1.00000\exp(3.00(\sin\theta/\lambda)^2)]/[\sigma^2(F_o^2) + 0.0000{*}P + (0.029P)^2]$, where $P = 0.33333F_o^2 + 0.66667F_c^2$	$w = 1/[\sigma^2(F_o^2) + (0.0821P)^2 + 0.0698P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	<0.0001	<0.0001	0.001
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.21, −0.28	0.19, −0.23	0.22, −0.37
Extinction method	*SHELXL*	*SHELXL*	*SHELXL*
Extinction coefficient	0.0146 (7)	0.0060 (3)	0.0108 (6)

Computer programs: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1989), *TEXSAN* (Molecular Structure Corporation, 1989), *SHELXS*86 (Sheldrick, 1990), *SHELXL*97 (Sheldrick, 1997), *PLATON* (Spek, 1998), *PARST*97 (Nardelli, 1996).

phosphite (2 mmol) was added, the reaction mixture was stirred for an additional 2 h and left to stand overnight at ambient temperature. The deposited crystals were isolated by filtration, washed with acetic acid (2 × 1 ml) and ethanol (2 × 1 ml) and dried in a vacuum desiccator over P_2O_5. Following this procedure (I)–(III) were obtained:

(I) (R = $PhCH_2CH_2$): yield 80%, m.p. = 418–420 K, $\delta(^{31}P)_{(CDCl_3)}$ = 17.7 p.p.m.;

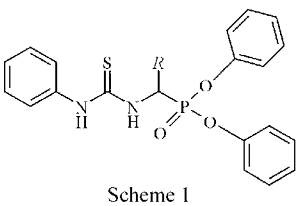
(II) (R = Ph): yield 85%, m.p. = 442–443 K, $\delta(^{31}P)_{(CDCl_3)}$ = 13.7 p.p.m.;

(III) (R = *tert*-Bu): yield 80%, m.p. = 454–455 K, $\delta(^{31}P)_{(CDCl_3)}$ = 16.9 p.p.m.

Compounds (I)–(III) were homogeneous on TLC (SiO_2/chloroform) and in ^1H NMR and ^{31}P NMR. The ^1H NMR and ^{31}P NMR spectra of all the title compounds were recorded on a Bruker AC 200 spectrometer operating at 200 MHz (for ^1H)

or 81.01 MHz (for ^{31}P). Microanalysis (C, H, N, P, S) of all the synthesized compounds agreed to within ±0.3% of the theoretical value. The melting points of the synthesized compounds (I)–(III) were determined on a Boetius apparatus and were not corrected.

The title compounds were crystallized by the slow evaporation of a chloroform–ethanol solvent system (1:1).



Scheme 1

Compound	Formula	Substituent *R*	Reference
(I)	$C_{28}H_{27}N_2O_3PS$	$PhCH_2CH_2-$	This work
(II)	$C_{26}H_{23}N_2O_3PS$	Ph	This work
(III)	$C_{24}H_{27}N_2O_3PS$	$(CH_3)_3C-$	This work
(IV)	$C_{24}H_{27}N_2O_3PS$	$(CH_3)_2CHCH_2-$	Chęcińska, Sieroń *et al.* (2003)
(V)	$C_{24}H_{27}N_2O_3PS$	$CH_3CH_2CH_2CH_2-$	Chęcińska, Grabowski & Małecka (2003)
(VI)	$C_{23}H_{25}N_2O_3PS$	$CH_3CH_2CH_2-$	Chęcińska, Grabowski & Małecka (2003)
(VII)	$C_{21}H_{21}N_2O_3PS$	CH_3-	Chęcińska, Grabowski & Małecka (2003)
(VIII)	$C_{24}H_{27}N_2O_3PS$	$CH_3CH_2(CH_3)CH-$	Chęcińska, Sieroń *et al.* (2003)
(IX)	$C_{23}H_{25}N_2O_3PS$	$(CH_3)_2CH-$	Chęcińska, Sieroń *et al.* (2003)

2.2. X-ray data

The single-crystal X-ray data for structures (I)–(III) are summarized in Table 1.[1] The unit-cell determination as well as all intensity measurements were carried out on an AFC5*S* Rigaku diffractometer (Molecular Structure Corporation, 1989) using Cu *Kα* radiation (λ = 1.54178 Å). The reflection intensities were collected at 293 (2) K and measured using the *ω* scan method. Three standard reflections monitored during data collection showed insignificant (<2%) intensity fluctuation. The data were corrected for Lorentz and polarization effects (*TEXSAN*; Molecular Structure Corporation, 1989). An analytical absorption correction was also applied (de Meulenaer & Tompa, 1965).

The structures were solved by direct methods using *SHELXS*86 (Sheldrick, 1990). In all cases the best E-maps revealed all the non-H atoms. Refinement of the structures was made by a full-matrix least-squares calculation based on F^2 using *SHELXL*97 (Sheldrick, 1997). All non-H atoms were refined with anisotropic displacement parameters. The amide H atoms were clearly revealed in the difference maps. Their atomic coordinates were refined with N—H distances restrained to a common value, while their $U_{\rm iso}$ values were refined freely. All other H-atoms were placed in geometrically idealized positions, with C—H distances in the range 0.93–0.98 Å, and constrained to ride on their parent C atom, with $U_{\rm iso}(H) = 1.2\ U_{\rm eq}(C)$ [or 1.5 $U_{\rm eq}(C)$ for the methyl groups].

3. Comment

3.1. Molecular geometry

The molecular structures of the three title (*N*-phenylthioureidoalkyl- and -aryl)phosphonates are presented in Figs. 1–3, respectively. The geometry of the thioureide group has recently attracted some interest (Allen *et al.*, 1997). It was shown that the S=C double bond may delocalize when the S

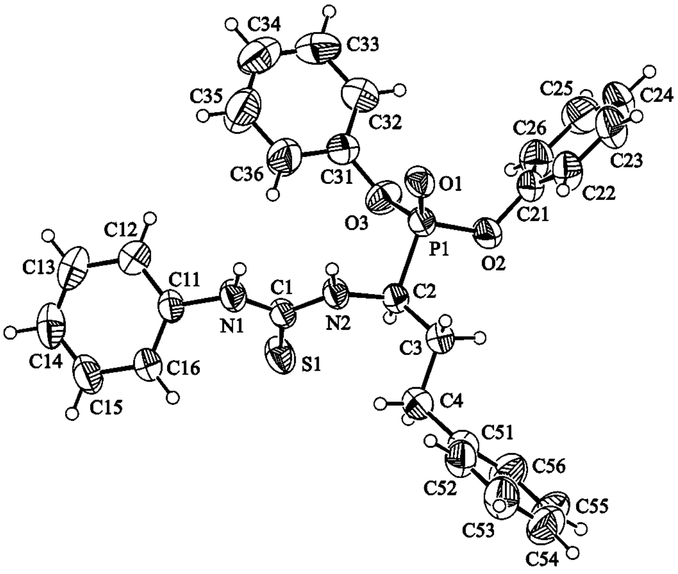


Figure 1
The molecular structure of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radius.

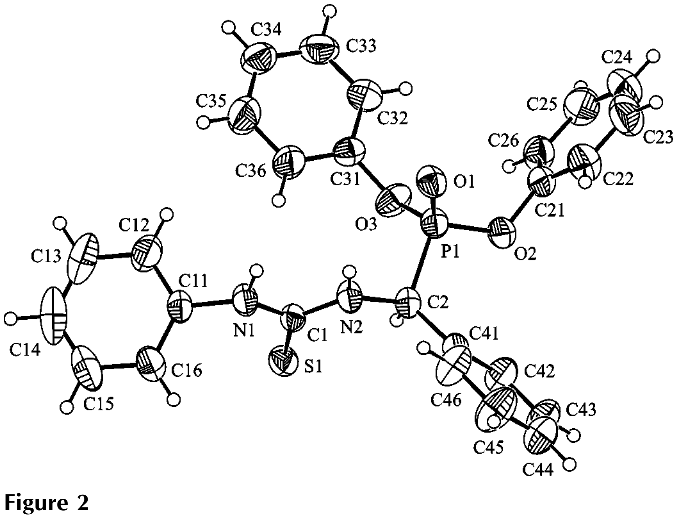


Figure 2
The molecular structure of (II) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radius.

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE5004). Services for accessing these data are described at the back of the journal. The CCDC reference numbers are as follows: 218518, 218519, 218520 for (I), (II) and (III), respectively.

Table 2
Selected geometric parameters (Å, °) for (I), (II) and (III).

	(I)	(II)	(III)
S1—C1	1.663 (2)	1.662 (3)	1.654 (2)
C1—N1	1.349 (3)	1.349 (3)	1.354 (3)
C1—N2	1.363 (3)	1.352 (3)	1.358 (3)
N1—C11	1.434 (3)	1.429 (3)	1.427 (3)
N2—C2	1.457 (3)	1.456 (3)	1.457 (3)
C2—P1	1.799 (2)	1.806 (3)	1.809 (2)
P1—O1	1.4680 (15)	1.4677 (19)	1.4668 (15)
P1—O2	1.5740 (16)	1.5757 (18)	1.5768 (15)
P1—O3	1.5691 (17)	1.5680 (19)	1.5774 (16)
S1—C1—N1	124.00 (17)	123.7 (2)	124.48 (16)
S1—C1—N2	123.53 (17)	123.5 (2)	123.14 (17)
N1—C1—N2	112.47 (19)	112.7 (2)	112.37 (19)
O1—P1—O2	115.74 (9)	116.08 (11)	114.28 (9)
O1—P1—O3	114.03 (9)	114.26 (11)	114.33 (9)
O1—P1—C2	114.59 (10)	114.70 (12)	116.32 (11)
O2—P1—O3	103.91 (10)	103.52 (11)	102.34 (9)
O2—P1—C2	101.63 (9)	102.91 (11)	104.31 (9)
O3—P1—C2	105.48 (10)	103.79 (12)	103.62 (10)
S1—C1—N1—C11	−4.5 (4)	−10.3 (4)	−8.1 (3)
S1—C1—N2—C2	9.0 (3)	6.9 (4)	−5.3 (3)

Table 3
Hydrogen-bonding geometry (Å, °) of N1—H1···O1 for (I), (II) and (III).

	N1—H1	H1···O1	N1···O1	N1—H1···O1	Symmetry code
(I)	0.82 (2)	2.06 (2)	2.861 (2)	163 (2)	$-x, -y, -z$
(II)	0.86 (2)	1.98 (2)	2.836 (3)	170 (3)	$-x, -y, -z$
(III)	0.85 (1)	2.19 (2)	2.976 (3)	153 (1)	$1-x, 1-y, 1-z$

Table 4
Hydrogen-bonding geometry (Å, °) of N2—H2···O1 for (I), (II) and (III).

	N2—H2	H2···O1	N2···O1	N2—H2···O1	Symmetry code
(I)	0.89 (2)	2.14 (2)	2.967 (3)	153 (2)	$-x, -y, -z$
(II)	0.84 (2)	2.27 (3)	3.033 (3)	151 (3)	$-x, -y, -z$
(III)	0.86 (1)	2.05 (1)	2.884 (3)	162 (1)	$1-x, 1-y, 1-z$

atom acts as a hydrogen-bond acceptor. The delocalization leads to the elongation of the S=C bond and the shortening of the C—N bond.

In derivatives (I) and (II) the S1=C1 bond distances are essentially the same as the mean value given for the non-hydrogen-bonded thioureides given by Allen *et al.* (1997): 1.663 Å (Table 2). The corresponding bond length in (III) is somewhat shorter, but still assumes a common value (see Fig. 4 in Allen *et al.*, 1997). The N1—C1 bond distances agree with the literature mean value of 1.351 Å to within experimental error. The N2—C1 bond distances are longer and are in the range 1.352 (3)–1.363 (3) Å.

The S=C and C—N bond lengths of the related compounds (IV)–(IX) (see Scheme 1) are similar to those of the title compounds (Chęcińska *et al.*, 2001*a*,*b*; Chęcińska, Sieroń *et al.*, 2003; Chęcińska, Grabowski & Małecka, 2003). The S atom does not accept a hydrogen bond in any of these structures. Nevertheless, a correlation between the decrease of the S1=C1 bond lengths and the elongation of the N—Csp^2 single-bond distances can be observed (correlation coefficient = 0.74). This is similar to the S=C *versus* N—C distance correlation reported by Allen *et al.* (1997) (coefficient = 0.77), which was ascribed to resonance-induced hydrogen bonding. Our data suggests that an S=C and N lone-pair delocalization occurs even in the absence of N—H···S=C hydrogen bonds.

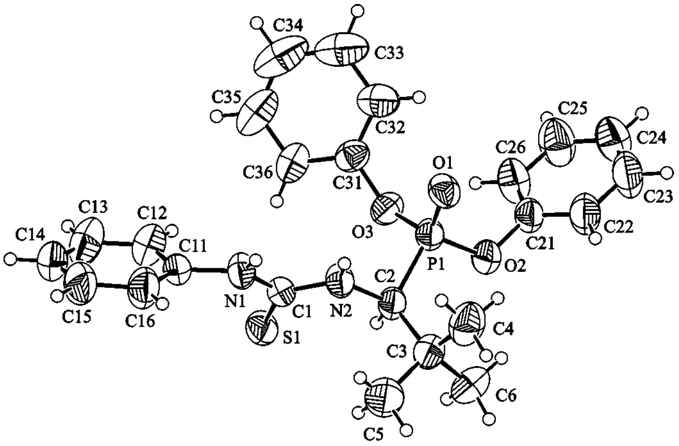

Figure 3
The molecular structure of (III) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radius.

The torsion angles S1—C1—N1—C11 and S1—C1—N2—C2 indicate that, as in the previously reported derivatives, the conformation of the thiourea fragment is *syn*–*syn* in all three title structures. To identify the preferred conformations, thiourea crystal structures (Fig. 4) were retrieved from the Cambridge Structural Database (CSD, Version 5.24, November 2002; Allen, 2002) and a sub-database of 39 error-free, ordered organic structures with $R < 0.07$ and e.s.d C—C ≤ 0.005 Å was created. Among these 39 structures, *syn*–*anti* or *anti*–*syn* conformations are dominant (24 examples). Only five thiourea groups adopt a *syn*–*syn* conformation. Meanwhile, among the 19 *N*-phenylthiourea derivatives, the phenyl substituent prefers a *syn* orientation with respect to the C=S bond (14 examples). It was found that the S—C—N valence angles can also be correlated with the conformation of the thiourea group. The S—C—N valence angles range from 116 to 121° for *anti*-oriented substituents and from 121 to 129° for the *syn* oriented ones. In the title (*N*-phenylthioureidoalkyl- and -aryl)phosphonates, the observed S1—C1—N1 and S1—

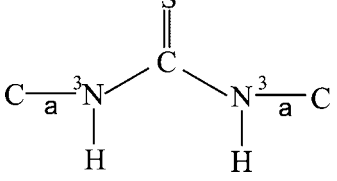

Figure 4
The fragment used to search thiourea compounds in the CSD. Superscripts 1 and 3 refer to the number of directly bonded atoms; 'a' represents an acyclic bond.

Table 5
Comparison of unit-cell parameters (Å, °) for (I)–(IX).

	Substituent	Space group	*a*	*b*	*c*	α	β	γ
(I)	PhEt	$P\bar{1}$	9.951 (1)	12.201 (1)	11.844 (1)	100.40 (1)	102.90 (1)	102.90 (1)
(II)	Ph	$P\bar{1}$	9.953 (1)	10.046 (1)	12.701 (1)	96.66 (1)	104.45 (1)	99.84 (1)
(IV)†	^{i}Bu	$P\bar{1}$	10.1931 (7)	10.5503 (5)	11.9560 (7)	90.932 (4)	103.252 (5)	101.923 (5)
(V)‡	^{n}Bu	$P\bar{1}$	9.953 (1)	10.841 (1)	11.734 (1)	92.64 (1)	102.38 (1)	103.82 (1)
(VI)§	^{n}Pr	$P\bar{1}$	9.873 (1)	10.626 (1)	11.709 (1)	91.39 (1)	102.44 (1)	104.57 (1)
(VII)¶	Me	$P\bar{1}$	9.753 (1)	10.069 (1)	12.255 (1)	98.17 (1)	103.37 (1)	111.63 (1)
(III)	*tert*-Bu	$P2_1/c$	10.688 (3)	9.888 (2)	22.961 (2)	90	97.79 (1)	90
(VII)††	*sec*-Bu	$P2_1/c$	9.9402 (4)	16.7505 (6)	14.1979 (5)	90	91.973 (3)	90
(IX)‡‡	^{i}Pr	$P2_1/c$	10.061 (1)	20.561 (1)	13.035 (2)	90	122.71 (1)	90

† Diphenyl [3-methyl-1-(3-phenylthioureido)butyl]phosphonate (Chęcińska, Sieroń *et al.*, 2003). ‡ Diphenyl 1-(3-phenylthioureido)pentylphosphonate (Chęcińska, Grabowski & Małecka, 2003). § Diphenyl 1-(3-phenylthioureido)butylphosphonate (Chęcińska, Grabowski & Małecka, 2003). ¶ Diphenyl 1-(3-phenylthioureido)ethylphosphonate (Chęcińska *et al.*, 2001*b*). †† Diphenyl [2-methyl-1-(3-phenylthioureido)butyl]phosphonate (Chęcińska, Sieroń *et al.*, 2003). ‡‡ Diphenyl [2-methyl-1-(3-phenylthioureido)propyl]phosphonate (Chęcińska, Sieroń *et al.*, 2003).

C1—N2 bond angles are all close to 123° so they confirm the above observation.

The geometry around the P atom is distorted tetrahedral in each reported structure. The deformations of the tetrahedra can be explained by the steric effect of the different substituents and bond types, *viz*. the double P1═O1 bond and single P1—C2 bonds. The changes in the corresponding P1—O1 and P1—O2 bond distances are small, only the lengthening of the P1—O3 bond in (III) is significant. The increase in the O1—P1—C2 and O2—P1—C2 angles and the decrease in the O3—P1—C2 angle also show the steric influence of the bulky *tert*-butyl group on the distortion of the tetrahedral environment of the P atom in (III).

3.2. Dimer formation

In each investigated structure the amide N1 and N2 atoms act as hydrogen-bond donors to the O1 atom of an inversion-related molecule (Tables 3 and 4), thus intermolecular N1—H1···O1 and N2—H2···O1 hydrogen bonds are formed. These bonds link characteristic centrosymmetric dimers (Fig. 5), which are present in all the crystal structures of (I)–(IX). The formation of the dimers may be responsible for the unusual *cis–cis* conformation of these compounds, since this arrangement ensures that the NH hydrogen atoms are not hindered sterically by the S atom.

In (I) and (II) the hydrogen bonds are complemented by a pair of edge-to-face π–π interactions between the phenyl moieties attached to the N1 and O2 atoms of the two molecules. [The centroid–centroid distances are 5.01 and 4.90 Å, the angles between the phenyl planes are 61 and 55° for (I) and (II), respectively.] A similar interaction can be observed between the phenyl rings of the C2 substituent and that bound to O3, although these moieties are further apart (5.70 and 5.09 Å).

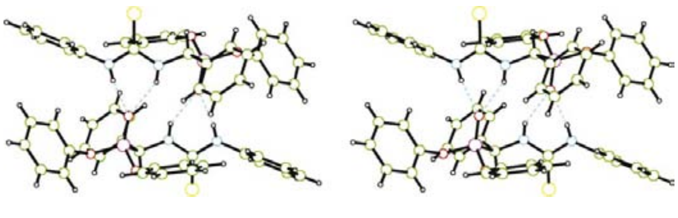

Figure 5
Stereoview of the hydrogen-bonded dimers in (III) [symmetry code: (i) $1-x, 1-y, 1-z$].

The phenyl rings have a markedly different orientation in the dimers of (III) (Fig. 5). The interaction between the substituents on N1 and O2 resembles an offset face-to-face interaction, but its geometry is far from ideal (centroid–centroid distance: 5.58 Å, interplanar angle: 26°). The third phenyl group of (III) caps the *tert*-butyl substituent and forms a van der Waals contact with it.

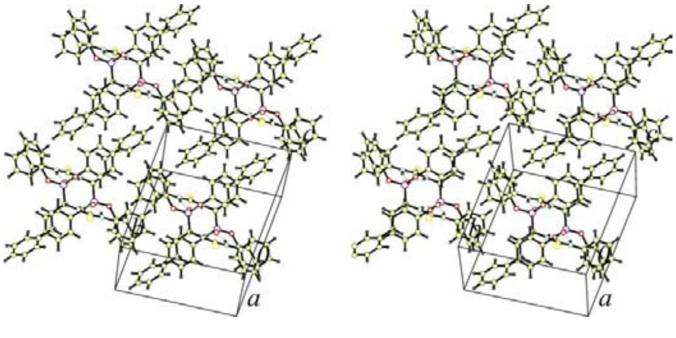

Figure 6
The crystal packing of (I).

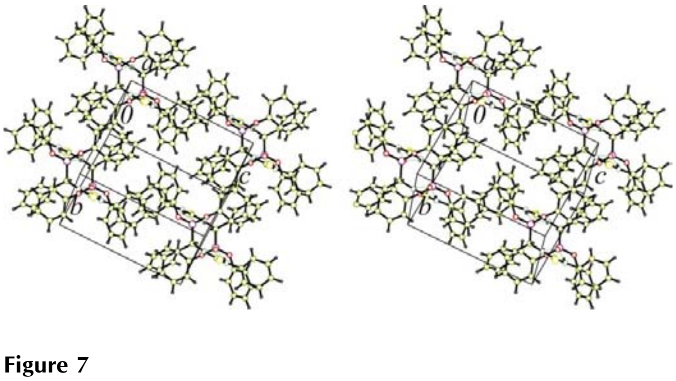

Figure 7
The crystal packing of (II).

Table 6
Descriptors of isostructurality, Π, I_v and $I_v^{\max}$, for possible pairs of crystals of analysed (*N*-phenylthioureidoalkyl- and -aryl)phosphonates.

	Π	I_v (%)	$I_v^{\max}$ (%)
Triclinic system			
(I)/(II)	0.036	74.8	96.2
(I)/(IV)	0.035	69.6	95.4
(I)/(V)	0.042	77.7	95.2
(I)/(VI)	0.052	75.5	93.6
(I)/(VII)	0.068	20.8	88.8
(II)/(IV)	0.002	68.2	99.1
(II)/(V)	0.005	70.8	98.9
(II)/(VI)	0.015	70.1	97.4
(II)/(VII)	0.030	20.2	92.7
(IV)/(V)	0.006	86.8	100.0
(IV)/(VI)	0.016	86.3	98.3
(IV)/(VII)	0.031	19.1	93.5
(V)/(VI)	0.010	93.4	98.5
(V)/(VII)	0.025	20.3	93.7
(VI)/(VII)	0.015	20.8	95.2
Monoclinic system			
(III)/(VIII)	0.063	27.3	100.0
(III)/(IX)	0.017	11.3	98.1
(VIII)/(IX)	0.045	30.0	98.0

3.3. Packing arrangements and isostructurality

The triclinic structures (I) and (II) (Figs. 6 and 7) were found to be isostructural. Their packing is characterized by edge-to-face interactions between the phenyl rings of translation-related dimers. Along the crystallographic *b* and *c* axes, the four-armed dimers are connected like cogwheels. Each arm (or cog) is embraced by two arms of a neighboring molecule in the same row or column.

A row of dimers is formed in (III) along the *b* axis (Fig. 8), similar to the rows along *c* in (I) and (II). These similar rows differ in the interactions of adjacent dimers. In (I) and (II) the arms containing the thioureide moiety are embraced by two arms of the next dimer. In (III) the arms with the C2-substituent are embraced instead. Another difference stems from the monoclinic symmetry of (III). Since neighboring rows in (III) are related by a screw axis parallel to the rows, they become antiparallel. The translation-related rows of (I) and (II) are, of course, parallel.

The observation of the above similarities and our previous results on the isostructurality of (*N*-phenylthioureidoalkyl)phosphonates (Chęcińska, Sieroń *et al.*, 2003) suggested a detailed comparison of the crystal structures of (I)–(IX). These (*N*-phenylthioureidoalkyl- and -aryl)phosphonates crystallize either with monoclinic $P2_1/c$ or with triclinic $P\bar{1}$ symmetry (Chęcińska *et al.*, 2001*a*,*b*; Chęcińska, Sieroń *et al.*, 2003; Chęcińska *et al.*, 2003). It was found that the packing arrangement of (I) and (II) is also exhibited by (IV), (V) and (VI). This means that the compounds with PhEt, Ph, ^{i}Bu, ^{n}Bu, and ^{n}Pr substituents form isostructural crystals [see (I)].

The degree of similarity among these compounds was quantified by the unit-cell similarity index Π (Kálmán *et al.*, 1993) [$\Pi = (a + b + c/a' + b' + c') - 1$, where a, b, c and a', b', c' are the orthogonalized lattice parameters] and by the volumetric isostructurality index I_v (percentage ratio of the overlapping volumes of the molecules in the analyzed structures to the average of the corresponding molecular volumes; Fábián & Kálmán, 1999). The results (Tables 5 and 6) show that the ^{n}Bu and ^{n}Pr derivatives (V) and (VI) display the closest similarity. The three common C atoms in the substituents of (IV) (^{i}Bu), (V) (^{n}Bu) and (VI) (^{n}Pr) exactly overlap in a least-squares fit of the corresponding molecules. This also holds for the first two atoms in the chain when comparing (VI) with (III), (VIII) or (IX). Therefore, the structure of (VI) is taken as a reference for the comparison.

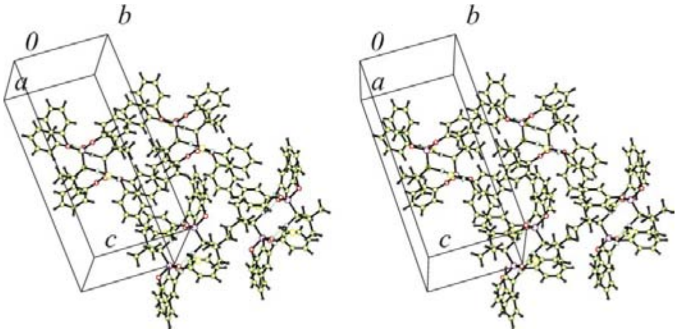

Figure 8
The crystal packing of (III).

As shown by the very high I_v index for (V)/(VI) (Table 6), the lengthening of the alkyl chain has only a small effect on the crystal structure. This can be understood from the shape of (VI) dimers (Fig. 9). The straight *n*-alkyl chain points radially outwards from the core of the dimer. It is parallel with the nearby O3 phenyl group and does not have close contact with any other group. Consequently, its elongation has little influ-

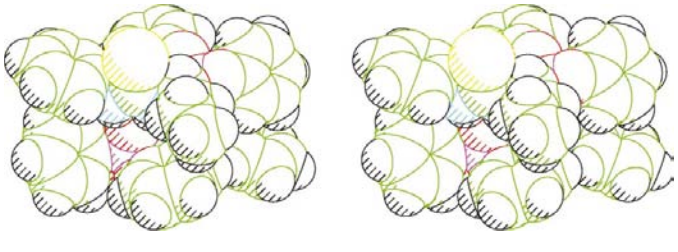

Figure 9
Space-filling model of the centrosymmetric dimer of (VI).

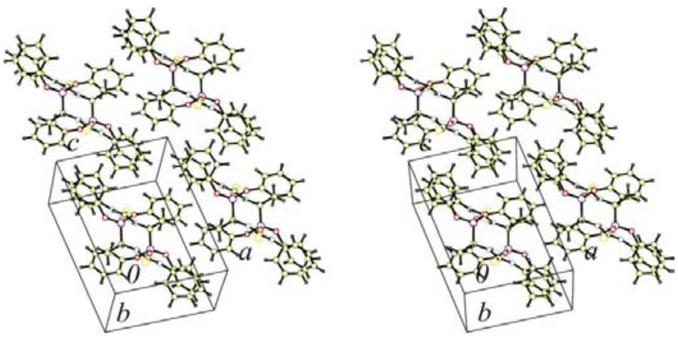

Figure 10
The crystal packing of (VII).

ence on the shape of the dimer and it does not hinder phenyl–phenyl interactions between adjacent dimers.

The effect of adding a branch to the propyl chain is bigger as shown by the I_v index for (IV)/(V.) A hydrogen at the second C atom of the *n*-propyl group is replaced by a methyl group in (IV). One of these H atoms is directed towards the thioureide group and is sterically hindered. Therefore, the additional methyl group in (IV) replaces the other hydrogen, which points upwards in Fig. 9. This changes the external surface of the dimer [compared with (V)] and causes a noticeable increase in the *a* axis (Table 5). (The new $C-CH_3$ bond is approximately parallel with the *a* axis.)

The isostructurality indices show that structure (I) is less similar to (V) than (IV) (Table 6). The I_v value for (I)/(V) being larger than that for (I)/(IV) indicates that the nature of the distortion from the reference structure is different in (I) and (IV). Indeed, the *b* axis is elongated in (I), but the *a* axis in (IV) (Table 5). The reason for a longer *b* axis is clear from the packing diagram of (I) (Fig. 6). The phenylethyl group protrudes parallel to this axis and increases the size of the (I) dimers.

Even though the unit-cell dimensions of (II) are similar to those of (V), the I_v index for this pair is smaller than for (I) and (V). This is apparently the consequence of their molecular constitutions. While the ethyl part and the first aromatic C atom of the PhEt substituent of (I) completely overlap with the ^{n}Pr moiety of (V), only one atom can be in an identical position in the substituents of (II) (Ph) and (V) (^{n}Pr).

The only compound that crystallizes with the space group $P\bar{1}$ without being isostructural with (I) and (II) is (VII) (R = Me). In this structure (Fig. 10), a similar grid of dimers is assembled to those of the other triclinic crystals. The shortening of the alkyl chain generates a hollow region on the surface of the dimers (*cf*. Fig. 9). In (VII) (Fig. 10) the 'methyl arms' of the dimers are inserted between two arms of the next molecule in the same row and the '*N*-phenyl arms' between the arms of the following molecule in the same column. The role of arms in holding together the rows and columns is the opposite in (I), (II) and (IV)–(VI). The unusual row structure of (VII) is stabilized by the interaction of 'upper' and 'lower' molecules of adjacent dimers. A shift perpendicular to the *ac* plane ensures that the hollows at the methyl groups are filled by the O3 phenyl moiety from the neighboring dimer.

Compounds (III), (VIII) and (IX) crystallize with the space group $P2_1/c$. It is a common feature of their molecules that the first C atom of their alkyl chain bears at least one branching methyl group. Nevertheless, the crystal structure of (III) is closer to that of (VII) than to (VIII) and (IX). Structures (III) and (VII) are built up from similar rows (Figs. 8 and 10), but the adjacent rows are antiparallel in (III) and parallel in (VII). Again the formation of these rows can be attributed to the shortness of the alkyl fragment.

The one-dimensional-isostructurality of (VIII) and (IX) has already been noted (Chęcińska, Sieroń *et al.*, 2003). Interestingly, this relationship can be extended to also include (I), (II), (IV), (V) and (VI). In all these seven structures, identical columns are built from the dimers (Figs. 6, 7 and 11). Columns are related to each other by translation in the triclinic structures and by screw axes with different relative orientations in (VIII) and (IX). The prevalence of the column motif suggests this to be the energetically preferred arrangement of dimers.

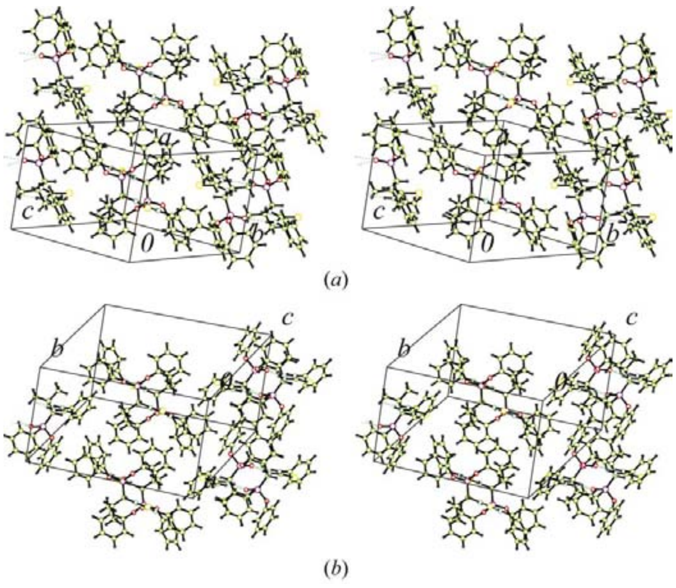

Figure 11
The crystal packing of (*a*) (VIII) and (*b*) (IX).

4. Conclusions

Three (*N*-phenylthioureidoalkyl- and -aryl)phosphonates have been synthesized and their crystal and molecular structures examined. The comparative analysis was carried out with literature data. It can be seen that the different packing arrangements of (*N*-phenylthioureidoalkyl- and -aryl)phosphonates are all based on the formation of characteristic dimers and can be described in terms of the packing of the dimers. In these arrangements common motifs were identified, which helped in understanding the relationship of molecular and crystal structures and in the identification of preferred interactions. The resemblances between the analyzed structures result in one-dimensional or three-dimensional isostructurality.

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