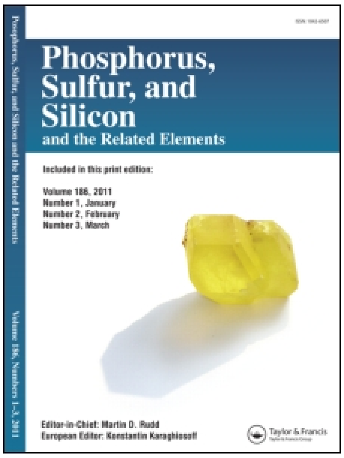

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N-PHOSPHORYLATED DIMETHYLSULFOXIMIDES. I. CRYSTAL AND MOLECULAR STRUCTURES

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N-PHOSPHORYLATED DIMETHYLSULFOXIMIDES. I. CRYSTAL AND MOLECULAR STRUCTURES

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Crystal and molecular structures of three *N*-phosphoryl dimethylsulfoximides, $(RO)_2P(O)-N=S(O)Me_2$ (**1**) have been determined by X-ray diffraction. The values for the P—N bond distances and for the PNS bond angles indicate that the P—N bond in (**1**) has a partial double bond character, similar to that observed in phosphoramidates. The mutual orientation of the P=O and N=S groups in (**1a**) (R = iPr) and (**1b**) (R = Ph) is close to *gauche*, while for the 5,5-dimethyl-2-oxo-2-amino-1,3,2-dioxaphosphorinane derivative (**1c**) this orientation is close to *anti*. The orientation between the P—N and S=O groups is in all substances nearly *gauche*. In the cyclic compound (**1c**) the phosphoryl oxygen is axial, contrary to the usual equatorial preference for the P=O group in 1,3,2-dioxaphosphorinane systems.

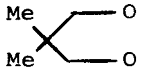
Recently developed synthetic methods[1] have made *N*-phosphorylated dimethylsulfoximides (**1**) easily available substances. Compounds (**1**), incorporating the OPNSO linkage into a single molecular framework, represent an interesting topic for structural and bonding studies. Using (**1**) as models, numerous problems, such as the geometry of the OPNSO molecular backbone, hybridization and bonding of nitrogen, conjugation effects, or secondary interactions, could be investigated. Structural characteristics of compounds (**1**) could then be compared with a variety of the related organophosphorus structures for which ample data on structure and bonding are available. To provide this information on system (**1**), an X-ray crystallographic analysis of substrates (**1a**)–(**1c**) was undertaken.

$(RO)_2P(O)-N=S(O)Me_2$

1 a, R = iPr

b, R = Ph

c, $(RO)_2$ =



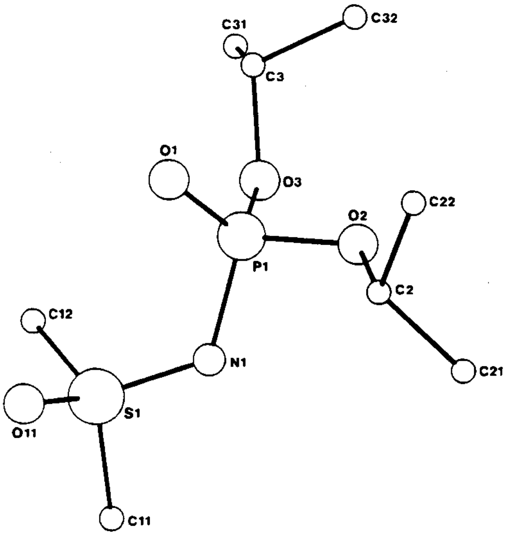


FIGURE 1 Perspective view (and atomic nomenclature) of the molecule of *N*-(diisopropylphosphoryl)dimethylsulfoximide (**1a**).

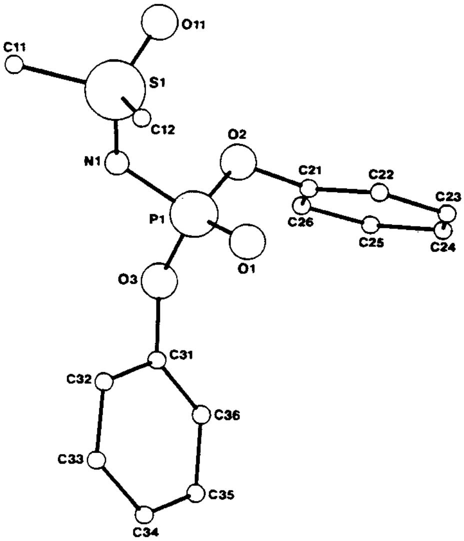


FIGURE 2 Perspective view (and atomic nomenclature) of the molecule of *N*-(diphenylphosphoryl)dimethylsulfoximide (**1b**).

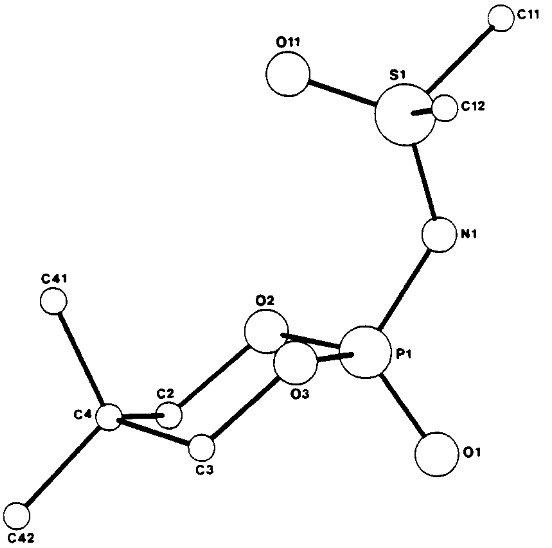


FIGURE 3 Perspective view (and atomic nomenclature) of the molecule of *N*-(2,2-dimethylpropylenephosphoryl)dimethylsulfoximide (**1c**).

RESULTS AND DISCUSSION

Perspective views of the molecules (**1a**)–(**1c**) with atomic nomenclature are presented in Figures 1–3; Table I lists selected molecular dimensions with standard deviations in parentheses.

Both phosphorus and sulfur centres in (**1**) are tetrahedral (bond angles averaging to 109.2° and 109.3°, respectively), indicating the absence of any significant secondary interactions that could have disturbed the tetrahedral geometry at these two acyl centres. However, the values of individual X—P—Y and Z—S—W bond angles deviate markedly from the ideal tetrahedral value according to the pattern analogous for both centres (Table II).

The bond angles shown in Table II follow the general trend observed for tetrahedral molecules, which results, among other factors, from the fact that multiple-bond orbitals repel other orbitals more strongly than do single bond orbitals.[2] For the P^{IV} derivatives the value of a X—P—Y angle can therefore serve as an approximate measure of the P—X and/or P—Y bond order and can be correlated with bond distances.[3] It follows from Table II that the bond order to phosphorus decreases in the sequence: phosphoryl > P—N > P—O (ester); for the sulfonyl centre this order is S═O > S═N > S—C. The important observation is that the P—N bond order in (**1**) is higher than that of the P—O (ester) bond; in fact this effect is very similar to that observed in phosphoramidates.[3]

In the OPNSO skeleton, only the sulfoxide bond distance is virtually constant (1.43 Å) for all three substrates confirming a lack of variation of S—O bond lengths (1.42–1.44 Å) in sulfonyl derivatives.[4] The remaining bonds show small, but measurable variations in their lengths; it is interesting to note however, that the sum of

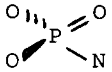
TABLE I

Selected bond lengths and angles for substrates (**1**)

	1a	**1b**	**1c**
Bond lengths (Å)			
P(1)—O(1)	1.454(7)	1.471(9)	1.463(4)
P(1)—O(2)	1.551(8)	1.599(10)	1.575(4)
P(1)—O(3)	1.581(7)	1.587(10)	1.591(4)
P(1)—N(1)	1.661(9)	1.598(11)	1.595(5)
N(1)—S(1)	1.503(9)	1.540(10)	1.536(5)
S(1)—O(11)	1.428(8)	1.429(11)	1.429(4)
S(1)—C(11)	1.720(10)	1.717(15)	1.731(6)
S(1)—C(12)	1.765(11)	1.741(14)	1.756(7)
Bond angles (°)			
O(3)—P(1)—O(2)	100.8(4)	100.2(5)	103.5(2)
O(3)—P(1)—O(1)	114.6(4)	114.3(6)	112.8(3)
O(2)—P(1)—O(1)	114.7(4)	113.8(5)	113.4(3)
O(3)—P(1)—N(1)	103.5(4)	103.4(6)	108.8(3)
O(2)—P(1)—N(1)	104.4(5)	102.8(5)	105.4(2)
O(1)—P(1)—N(1)	116.9(5)	119.9(6)	112.3(3)
P(1)—N(1)—S(1)	123.8(6)	126.0(7)	128.5(3)
N(1)—S(1)—O(11)	119.3(5)	118.0(7)	119.2(3)
N(1)—S(1)—C(11)	103.9(6)	105.0(8)	104.0(3)
N(1)—S(1)—C(12)	111.3(6)	110.4(8)	109.1(3)
O(11)—S(1)—C(11)	109.9(6)	109.1(8)	110.6(3)
O(11)—S(1)—C(12)	107.8(6)	109.0(8)	109.2(3)
C(11)—S(1)—C(12)	103.5(6)	104.5(8)	103.5(3)
Torsional angles (°)			
O(1)—P(1)—N(1)—S(1)	36.80	48.89	−164.36
P(1)—N(1)—S(1)—O(11)	−69.84	63.36	−37.76

TABLE II

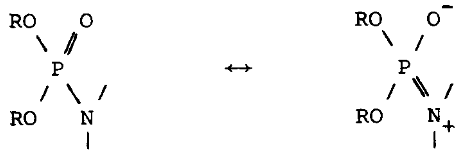
Deviations from ideal tetrahedron for the P and S bonds in (**1**)

	o^{a}	n^{b}		o^{a}	n^{b}
N—P=O	116.4 ± 3.8	3	N=S=O	118.8 ± 0.7	3
O—P=O	113.9 ± 0.7	6	C—S=O	109.3 ± 0.9	6
O—P—N	104.7 ± 2.2	6	C—S=N	107.3 ± 3.4	6
O—P—O	101.5 ± 1.7	3	C—S—C	103.8 ± 0.6	3
	av. 109.2 ± 6.2			av. 109.3 ± 5.1	

[a] Average value for (**1a**)–(**1c**).

[b] Number of bond angles used for the calculation.

the distances for all the four bonds involved remains remarkably constant (6.04, 6.04 and 6.03 Å, respectively). The P—N bond distances obtained for substrates (**1**) are well below the value of 1.78 Å, considered as that for the "pure" single P—N bond.[5] The observed values of 1.60–1.66 Å for the P—N bonds in (**1**) correspond closely to the range of 1.61–1.65 Å reported for a variety of phosphoramidates (**2**),[6] for which a certain degree of p_π–d_π bonding between nitrogen and phosphorus has to be taken into account (resonance structure **2A**).[7]



2 **2a**

In fact, the P—N bond distances in (**1b**) and (**1c**) (1.60 Å) reach the same value as that reported for the P—N bond in sulfimidophosphonium salt (**3**)[8] which is regarded as a heteroallenic system with the full p_π–d_π P—N bonding.

$$Ph_3P{=}\overset{+}{N}{=}SPh_2\ SbCl_6^-$$

3

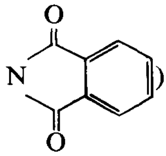
In (**3**) the PNS linkage was found to be fully symmetrical (P—N = N—S = 1.60 Å) indicating symmetrical charge delocalization within this triatomic group. In substrates (**1**), the P—N bond is always longer than the N—S bond, in accordance with the conventional structural formula of (**1**) which implies a higher bond order between nitrogen and sulfur than between nitrogen and phosphorus. Although any value suggested as a bond distance for a "pure" phosphorus–nitrogen double bond must be treated with caution,[9] there is little doubt about the N → P back donation effect in (**1**):

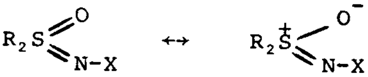
$$(RO)_2P(O){-}N{=}S(O)Me_2 \leftrightarrow (RO)P(O^-){=}\overset{+}{N}{=}S(O)Me_2$$

1 **1a**

The bonding represented by structure (**1A**) requires not only the shortening of the P—N distance, but should also result in a change of the geometry at the nitrogen atom. Structure (**1**) involves trigonal nitrogen, hence the P—N—S bond angle of 120°, while the allenic nitrogen in structure (**1A**) requires a linear arrangement of the PNS atoms.

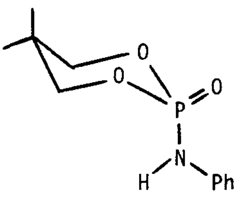
The values of the P—N—S angle in substrates (**1a**)–(**1c**) are 123.8, 126.0 and 128.5° respectively, which are greater than 123.6° reported for ions (**3**),[8] and which indicate significant widening of the bonds at nitrogen beyond the normal value for the trigonal geometry.[12]

The comparison of the sulfoximide part of molecules (**1**) with similar sulfur derivatives is difficult because of the scarcity of structural data on the $R_2S(O){=}NX$ system. The only available information relates to the single unsubstituted sulfoximide (X = H),[13] and to three *N*-phtalimido derivatives (X = ).[14] The molecular parameters reported for these compounds are generally in agreement with those obtained in this work for substrates (**1**). The only significant difference between (**1**) and compounds $R_2S(O)NX$ (X = H, phtalimido) concerns the S=O bond length; while in (**1**) a constant value of 1.43 Å was observed, the compounds reported in the literature[13,14] exhibit an S—O bond distance in the range of 1.44–1.48 Å. These variations are probably the result of differing electronic effects emanating from substituents at nitrogen. Relative to the phosphoryl group in (**1**), moieties such as hydrogen or phtalimido increase the contribution of the dipolar structure of the sulfoxide bond:

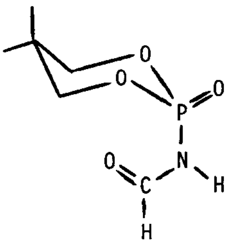


The *N*-phosphorylated sulfoximide system (**1**) consists of the nitrogen atom attached to the phosphorus and sulfur atoms, each of them of tetrahedral geometry, and each introducing a highly polar functional group (P=O and S=O, respectively). The observed geometry of the molecule of (**1**) should therefore be a result of the bonding requirements at nitrogen, dipole-dipole interactions between the P=O and S=O groups, and steric interactions between the two tetrahedral P^{IV} and S^{IV} centres. The relevant torsional angles for the molecular backbone of (**1**) are given in Table I. The OPNS torsional angles for (**1a**) and (**1b**) indicate a nearly *gauche* relation of the phosphoryl oxygen and sulfur atom. This arrangement removes the bulky tetrahedral group $S(O)Me_2$ from the vicinity of phosphate ester groups, thus avoiding any interactions between this group and the *i*-propoxy or phenoxy functions in (**1a**) and (**1b**). In compound (**1c**), in which the geometry of the phosphate ester groups is restricted by the 1,3,2-dioxaphosphorinan ring, a nearly *anti* relation of the P=O and N=S groups is attained (OPNS torsional angle of 164°). The torsional angles involving the PNSO linkage are for all substrates (**1**) in the range of 38° to 70°, i.e. the orientation of the S=O and N—P functions is not far from *gauche*. This result indicates that the *gauche* interactions between the tetrahedral phosphoryl moiety $P(O)(OR)_2$ and the (S)=O plus one (S)—Me group are more favourable than the similar interactions with two (S)—Me groups (PNSO torsional angle of *ca.* 180°).

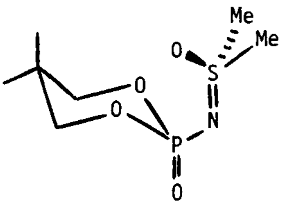
Structure of (**1c**) can be compared with molecular structures of two other 5,5-dimethyl-2-oxo-2-amino-1,3,2-dioxaphosphorinanes:N-phenyl (**4a**)[15] and N-formyl (**4b**)[16] derivatives. The projections of these three 1,3,2-dioxaphosphorinanes are shown below.



4a



4b

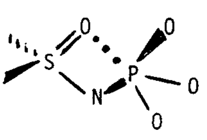


1c

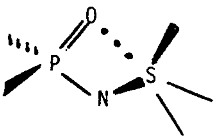
In both amide (**4a**) and imide (**4b**) the phosphoryl oxygen occupies the equatorial position, in agreement with the generally observed[17] conformational preference of the 2-substituted 1,3,2-dioxaphosphorinan-2-ones. This is the result of the short

P=O bond length which would bring the O atom and two axial hydrogen atoms at the C(4) and C(6) carbon atoms close together if the P=O group were to occupy an axial position. In this respect, molecule (**1c**), with axial location of the phosphoryl oxygen, is an exception. This change in the geometry at the exocyclic substituents at phosphorus can be due to two factors. Firstly, the P—N distance in (**1c**) ($\leqslant$ 1.60 Å) is considerably shorter than the P—N bonds in (**4a**) and (**4b**) (1.65 and 1.70 Å, respectively), which makes nitrogen more susceptible to the 1,3-steric interactions with the ring hydrogens. Secondly, both *N*-substituents in (**4a**), (**4b**) are planar (formyl and phenyl group), while nitrogen in (**1c**) is bonded to the tetrahedral group, which when located in the axial position would interact with ring hydrogens irrespective of other conformational angles.

The near-*gauche* orientation of the sulfoxide group with respect to the N—P bond opens the way for possible secondary interactions between the electron-rich oxygen of the S=O group and the electrophilic phosphorus (structure **5**).



5



6

The values of the non-bonding (S)O...P distances in (**1a**)–(**1c**) are 4.31, 3.42 and 3.33 Å, respectively; the corresponding sum of the Van der Waals radii is 3.30 Å. The analogous long-range interactions between the phosphoryl oxygen and the electrophilic sulfur atom (structure **6**) are possible only for (**1a**) and (**1b**) (in **1c** the phosphoryl group has an *anti* orientation with respect to the N=S bond). The observed (P)O...S distances are 3.26 Å for (**1a**) and 3.40 Å for (**1b**); the corresponding sum of the Van der Waals radii is 3.25 Å. Clearly there is no evidence for any significant donor-acceptor interactions between the S=O and P=O functional groups in substrates (**1**) (with perhaps an exception of the P=O...S=O contact in **1a**, where the interatomic distance approximates the distance determined by the sum of the Van der Waals radii). This result contrasts with the behaviour of N-benzoyldimethylphosphoramidate, $(MeO)_2P(O)$—NH—C(O)Ph, where the close contact between the phosphoryl oxygen and carbonyl carbon, P=O...C=O (O...C = 2.97 Å; sum of the Van der Waals radii 3.30 Å) has been observed.[18] The difference with regard to the intramolecular interactions could suggest a lower flexibility of the P—N=S bridge in (**1**) relative to that of the P—NH—C linkage in the mixed phosphoric-carboxylic imides.

EXPERIMENTAL

Substrates (**1**) were prepared as described before.[1] Compound (**1a**) crystallized as thin colourless needles (mp = 66–68°C).

For compounds (**1b**) and (**1c**) further recrystallizations from a mixture of petroleum spirit (80–100°C) and chloroform were required in order to produce suitably sized transparent needles (Compound (**1b**); mp = 91–92°C) and colourless rectangular-shaped crystals (Compound (**1c**); mp = 126°C) respectively. The crystal densities were determined by flotation.

TABLE III

Crystal data and experimental and refinement parameters for the structure analyses

Compound	(1a)	(1b)	(1c)
Molecular formula	$C_8H_{20}NO_4PS$	$C_{14}H_{16}NO_4PS$	$C_7H_{16}NO_4PS$
Molecular weight	257.3 g mol^{-1}	325.32 g mol^{-1}	241.25 g mol^{-1}
Space group	$P2_1/c$	$P2_12_12_1$	$P\bar{1}$
a	13.486(6) Å	8.857(2) Å	6.5220(4) Å
b	9.132(4) Å	10.682(3) Å	7.600(3) Å
c	10.815(13) Å	16.120(4) Å	11.762(1) Å
α	90°	90°	89.77(2)°
β	98.36(6)°	90°	100.673(8)°
γ	90°	90°	93.16(2)°
Z	4	4	2
V	1317.76 $Å^3$	1525.12 $Å^3$	572.05 $Å^3$
D_m	1.28 g cm^{-3}	1.40 g cm^{-3}	1.39 g cm^{-3}
D_c	1.30 g cm^{-3}	1.42 g cm^{-3}	1.40 g cm^{-3}
μ(Mo-K_α)	3.12 cm^{-1}	2.79 cm^{-1}	3.57 cm^{-1}
F(000)	552	680	256
Data collection			
Crystal dimensions	0.18 × 0.16 × 0.33 mm	0.11 × 0.25 × 0.5 mm	0.16 × 0.19 × 0.11 mm
Scan mode	$\omega - 2\theta$	$\omega - 2\theta$	$\omega - 2\theta$
Scan width ($\Delta\omega$)	$(1.37 + 0.35 \tan\theta)°$	$(0.40 + 0.35 \tan\theta)°$	$(0.74 + 0.35 \tan\theta)°$
Aperture width	$(1.73 + 1.05 \tan\theta)$ mm	$(1.10 + 1.05 \tan\theta)$ mm	$(1.13 + 1.05 \tan\theta)$ mm
Range scanned	$1 \leqslant \theta \leqslant 25°$	$1 \leqslant \theta \leqslant 25°$	$1 \leqslant \theta \leqslant 25°$
Stability of standard reflections	1.28%	1.74%	1.25%
Number of reflections collected	2610	1575	2117
Number of 'observed' reflections with I(rel) > 2σI(rel)	998	734	1436
Final refinement			
Number of variables	156	118	141
$R = \Sigma\lvert\lvert Fo\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert Fo\rvert$	8.37%	7.12%	6.85%
$Rw = \Sigma w^{\frac{1}{2}}\lvert\lvert Fo\rvert - \lvert F_c\rvert\rvert/\Sigma w^{\frac{1}{2}}\lvert Fo\rvert$	8.15%	6.65%	7.89%
Weighting scheme w	$1/\sigma^2F + 0.002F^2$	$1/\sigma^2F$	$1/\sigma^2F + 0.002F^2$

For each compound, single crystals were selected under the polarising microscope and reflection data at room temperature were obtained on an Enraf-Nonius CAD4 single crystal diffractometer.

The unit cell dimensions were obtained by a least-squares fit of the w, θ, K and ϕ angles of a number of reference reflections and are given in Table III along with the other pertinent crystallographic data.

Lorentz-polarisation corrections were applied to all data immediately after their collections, but absorption corrections were not.

Solution and Refinement. The structures were all solved by a preliminary direct methods routine of the new SHELXS-84 program system.[19] E-maps yielded the positions of virtually all the non-hydrogen atoms in each of the three structures. After a few cycles of least-squares refinement, difference electron-density maps were calculated and the positions of the remaining non-hydrogen atoms were revealed. Subsequent difference electron-density maps located the positions of all the hydrogen atoms.

For compounds (**1a**) and (**1c**), the final refinement was carried out with all the non-hydrogen atoms treated anisotropically, with the methyl hydrogen atoms refined as rigid groups and the remaining hydrogen atoms all constrained at 1.00 Å from their respective carbon atoms, their positions dictated by the geometry of the molecule.

However for compound (**1b**) in the final refinement only the phosphorus atom, its three oxygen ligands and the sulfur atom were treated anisotropically. The hydrogen atoms were refined as indicated above. Upon reversing all atomic coordinates, the final refinement yielded an identical R values and therefore we could not establish the absolute configuration of the molecule in this way.

TABLE IV

Fractional atomic coordinates ($\times 10^4$) with e.s.d's in parentheses for compound (**1a**)

Atom	*x/a*	*y/b*	*z/c*	Atom	*x/a*	*y/b*	*z/c*
S1	5913(2)	1463(3)	2430(2)	H121	5803(9)	2758(14)	577(10)
P1	7260(2)	3695(3)	3268(3)	H122	5018(9)	3418(14)	1450(10)
O1	6575(6)	4459(9)	3966(6)	H123	4772(9)	1872(14)	709(10)
O2	8356(6)	3597(8)	3940(7)	H2	7955(10)	2446(14)	5467(11)
O3	7425(6)	4463(8)	2003(6)	H211	9536(12)	1305(17)	5984(16)
O11	5240(6)	1356(9)	3330(7)	H212	9991(12)	2196(17)	4884(16)
N1	6967(7)	1984(10)	2838(8)	H213	8989(12)	1186(17)	4538(16)
C11	6066(10)	−228(12)	1783(11)	H221	9069(11)	3905(17)	7030(13)
C12	5317(9)	2501(14)	1157(10)	H222	8248(11)	4770(17)	6032(13)
C2	8555(10)	2940(14)	5212(11)	H223	9427(11)	4756(17)	5843(13)
C21	9362(12)	1850(17)	5180(16)	H3	6796(10)	6507(12)	2215(11)
C22	8876(11)	4173(17)	6130(13)	H311	7237(13)	7360(16)	698(12)
C3	7354(10)	6051(12)	1833(11)	H312	6539(13)	6141(16)	−120(12)
C31	7187(13)	6308(16)	440(12)	H313	7758(13)	6057(16)	−17(12)
C32	8309(12)	6732(15)	2474(14)	H321	8254(12)	7779(15)	2201(14)
H111	5405(10)	−655(12)	1418(11)	H322	8929(12)	6291(15)	2227(14)
H112	6425(10)	−927(12)	2405(11)	H323	8342(12)	6680(15)	3403(14)
H113	6479(10)	−47(12)	1102(11)				

TABLE V

Fractional atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$) with e.s.d's in parentheses for compound (**1b**)

Atom	*x/a*	*y/b*	*z/c*	Atom	*x/a*	*y/b*	*z/c*
S1	−506(4)	5959(4)	3495(3)	C35	983(18)	6516(13)	7939(11)
P1	1074(4)	5713(4)	4988(3)	C36	1218(15)	5817(13)	7225(8)
O1	1838(10)	6933(8)	5033(6)	H111	−2952(17)	6005(18)	3700(11)
O2	2148(10)	4593(9)	4696(5)	H112	−2512(17)	4739(18)	3186(11)
O3	524(12)	5186(7)	5857(6)	H113	−2676(17)	6073(18)	2699(11)
O11	470(13)	5383(10)	2901(7)	H121	−1177(19)	7981(13)	3726(10)
N1	−374(12)	5544(10)	4406(6)	H122	−509(19)	7662(13)	2806(10)
C11	−2348(17)	5663(18)	3227(11)	H123	643(19)	7998(13)	3565(10)
C12	−329(19)	7578(13)	3416(10)	H22	4643(16)	5941(13)	4647(9)
C21	3566(14)	4356(14)	5087(9)	H23	7012(20)	5384(16)	5264(9)
C22	4752(16)	5151(13)	4975(9)	H24	7268(19)	3543(14)	6055(9)
C23	6118(20)	4824(16)	5339(9)	H25	5176(16)	2139(15)	6197(10)
C24	6278(19)	3750(14)	5790(9)	H26	2750(17)	2708(14)	5640(9)
C25	5050(16)	2943(15)	5886(10)	H32	−1491(16)	6936(14)	6056(10)
C26	3653(17)	3255(14)	5552(9)	H33	−1979(19)	8143(16)	7283(10)
C31	337(15)	5941(13)	6555(9)	H34	−350(18)	7836(14)	8476(10)
C32	−853(16)	6822(14)	6562(10)	H35	1656(18)	6419(13)	8433(11)
C33	−1130(19)	7526(16)	7269(10)	H36	2067(15)	5200(13)	7212(8)
C34	−163(18)	7340(14)	7960(10)				

TABLE VI

Fractional atomic coordinates ($\times 10^4$) with e.s.d's in parentheses for compound (**1c**)

Atom	*x/a*	*y/b*	*z/c*
S1	1804(2)	11965(2)	6792(1)
P1	2586(2)	8349(2)	6942(1)
O1	1665(7)	6733(6)	6340(4)
O2	2856(6)	8220(5)	8298(3)
O3	4892(6)	8837(6)	6737(3)
O11	3147(9)	12521(6)	7846(4)
N1	1190(8)	9994(6)	6592(5)
C11	−566(11)	12943(10)	6644(7)
C12	2861(10)	12790(10)	5615(6)
C2	4468(9)	7071(8)	8878(5)
C3	6454(9)	7670(9)	7294(5)
C4	6601(8)	7679(8)	8614(5)
C41	7292(10)	9500(10)	9090(6)
C42	8152(12)	6311(11)	9142(7)
H111	−282(11)	14246(10)	6734(7)
H112	−1425(11)	12511(10)	7221(7)
H113	−1344(11)	12666(10)	5844(7)
H121	2091(10)	12593(10)	4804(6)
H122	4120(10)	12070(10)	5755(6)
H123	3308(10)	14066(10)	5732(6)
H21	4521(9)	7118(8)	9732(5)
H22	4109(9)	5834(8)	8593(5)
H31	6071(9)	6446(9)	6991(5)
H32	7843(9)	8072(9)	7114(5)
H411	7370(10)	9441(10)	9946(6)
H412	6361(10)	10453(10)	8764(6)
H413	8723(10)	9763(10)	8919(6)
H421	9616(12)	6555(11)	9017(7)
H422	7716(12)	5047(11)	8959(7)
H423	8083(12)	6561(11)	9968(7)

As is evident from a comparison of the final R values, the model for structure (**1a**) is not as good as those obtained for the other two. We ascribe this to crystal quality. A wide mosaic spread for compound (**1a**) manifests itself in relatively large values for the scan and aperture widths (see Table III).

Details of the final refinements are listed in Table III. Final fractional atomic coordinates and temperature factors are given in *Tables IV, V and VI*[20].

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