

Fig. 2. Packing diagram projected on the *bc* plane showing the intermolecular hydrogen bond (dotted lines).

system of the succinimide chromophore induced by the carbonyl oxygen O(4).

The nitrogen N(1) is the only hydrogen donor atom present in this molecule and it is hydrogen bonded to O(1) of a screw related molecule with an N(1)···O(1') separation of 2.961 (3) Å as shown in the crystal packing reported in Fig. 2. The presence of only one

intermolecular hydrogen bond and the absence of other short intermolecular contacts correlates well with the rather large temperature factors and the relatively low value of the crystal density compared with those of related structures.

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## Structure of Cytidinium Dihydrogenphosphate

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**Abstract.**  $C_9H_{14}N_3O_5^+ \cdot H_2PO_4^-$ ,  $M_r = 341.2$ , orthorhombic,  $P2_12_12_1$ ,  $a = 9.653$  (1),  $b = 7.0256$  (9),  $c = 19.873$  (2) Å,  $V = 1347.8$  (3) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.68$  g cm<sup>-3</sup>,  $\lambda(\text{Mo K}\alpha) = 0.71069$  Å,  $\mu = 2.04$  cm<sup>-1</sup>,  $F(000) = 712$ ,  $T = 291$  K,  $R = 0.030$  for 1198 observed reflexions. The ribose conformation is characterized by  $P = 163.9$  (8)° (<sup>2</sup>*E*) and  $\tau_m = 40.0$  (6)°. The glycosidic torsion angle  $\chi$  is in the *anti* region but has a very low value [34.4 (3)°]. The side chain has the preferred *gauche*<sup>+</sup> conformation [ $\gamma = 46.6$  (4)°]. The structure contains infinite ribose···phosphate chains in which the dihydrogenphosphate anions are hydrogen-bonded (*via* their POH donors) to O(3') and O(5')

neighboring nucleosides. The ribose···phosphate backbone is further reinforced by a direct O(5')H···O(2') bond between adjacent sugar residues. There are also analogous nucleobase···phosphate hydrogen-bonded chains in which the cytosinium cation is a threefold donor [N(4)H<sub>2</sub> and the N(3)H protonation site] and the phosphate anion is the acceptor. The hydrogen-bonded columns (along *b*) of anions and cations form pleated sheets which are further connected by an O(3')H···OP hydrogen bond.

**Introduction.** The present work continues a series of investigations into the factors influencing dimensions

and molecular interactions of nucleosides. In our earlier papers the effects of base modification and protonation in both cytidine (Jaskólski, Krzyżosiak, Sierzputowska-Gracz & Wiewiórowski, 1981; Krzyżosiak, Jaskólski, Sierzputowska-Gracz & Wiewiórowski, 1982; Kozerski, Sierzputowska-Gracz, Krzyżosiak, Bratek-Wiewiórowska, Jaskólski & Wiewiórowski, 1984) and adenosine (Jaskólski, 1982*a,b*, 1984) series have been discussed. In those papers protonation of parent and chemically modified cytidine and adenosine nucleosides was achieved using hydrochloric acid. Later, we reported on N-methylated rather than N-protonated cytidinium cations in their crystal structures with chloride (Jaskólski & Alejska, 1985) and nitrate (Jaskólski & Wiewiórowski, 1987) anions. Those studies were then extended to include the problem of the influence of different counteranions on the conformation and hydrogen-bonding properties of nucleoside cations (Wiewiórowski, Bratik-Wiewiórowska, Alejska, Perkowska, Krzyżosiak, Jaskólski & Rychlewska, 1986). This complicated problem is of basic importance to structural chemistry of nucleosides and deserves a very careful study. However, the amount of structural data is rather limited here as the nucleoside cations have been mostly studied in chloride salts. In the case of cytidine the crystal structure of cytidinium nitrate is also available (Guy, Nassimbeni, Sheldrick & Taylor, 1976). To introduce new anions into this discussion, the present paper reports the X-ray structure of cytidinium dihydrogenphosphate. This salt is particularly interesting as the two building blocks of nucleotides – the nucleoside and the phosphate residue – coexist here as separate ions. It provides, therefore, an illustration of the mutual interactions of these residues when they are not linked by the ester bond. Although a number of structures of esterified cytidine phosphates are known (acids, salts and complexes of both 3'- and 5'-isomers) this is the first example of a phosphate *salt* of a nucleoside.

In this context it may be appropriate to mention that the role of counteranions has also been recognized in other areas related to nucleic acids and their constituents. In a recent paper Hamori & Jovin (1987) reported on specific anionic ( $\text{ClO}_4^-$ ) interactions in  $\text{Mg}(\text{ClO}_4)_2$ -induced B–Z conformational transitions in DNA. Also, the conformational and hydrogen-bonding properties of biogenic polyamines (Jaskólski & Wiewiórowski, 1986) as well as their stabilizing effect on secondary and tertiary structures of nucleic acids (Barciszewski, Bratek-Wiewiórowska, Górnicki, Naskręt-Barciszewska, Wiewiórowski, Zielenkiewicz & Zielenkiewicz, 1988) seem to be greatly influenced by the character of the counteranion which is present in the system.

**Experimental.** Suitable crystals from water–methanol solution, crystal  $0.25 \times 0.3 \times 0.5$  mm, Syntex P2<sub>1</sub>

diffractometer, graphite monochromator, Mo K $\alpha$  radiation. Cell parameters from least-squares treatment of setting angles of 15 reflexions ( $13 < 2\theta < 25^\circ$ ).  $\theta:2\theta$  profiles measured for 1422 unique  $+h+k+l$  reflexions with  $2\theta < 50^\circ$  [ $\max.(\sin\theta)/\lambda = 0.595 \text{ \AA}^{-1}$ ] and with  $0 \leq h \leq 11$ ,  $0 \leq k \leq 8$ ,  $0 \leq l \leq 23$ ; profile analysis according to Lehmann & Larsen (1974). Random intensity variation (within 4.7%) of two standard reflexions measured every 1.5 h. No absorption correction. 1198 observed reflexions with  $I \geq 2\sigma(I)$ . The  $\text{PO}_4$  group and the cytosinium system located in an *E* map generated by *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); remaining non-H atoms located from a difference Fourier map. Full-matrix least-squares refinement on  $F$ ,  $w = \sigma^{-2}(F)$ . H atoms at C(5), C(6) and C(5') generated geometrically and riding on their carriers; remaining H atoms located in a  $\Delta F$  map and included in the refinement. All thermal parameters (anisotropic for non-H atoms, isotropic for H atoms) included in the refinement.  $F_c$  multiplied by  $(1 - xF_c^2/\sin\theta)$  with  $x$ , the empirical isotropic extinction parameter, refined to  $63(3) \times 10^{-8}$ . Final  $R = 0.030$ ,  $wR = 0.029$ ,  $S = 3.96$ ,  $(\Delta/\sigma)_{\max} = 0.63$ ; largest peak in final  $\Delta F$  map =  $0.18 \text{ e \AA}^{-3}$ , largest trough =  $-0.20 \text{ e \AA}^{-3}$ . Computer programs: *MULTAN80* (Main *et al.*, 1980), *SHELX76* (Sheldrick, 1976) and local programs (Jaskólski, 1982*c*), molecular illustrations drawn using *ORTEP* (Johnson, 1976) and *PLUTO* (Motherwell & Clegg, 1978). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

**Discussion.** Atomic coordinates are listed in Table 1.\* Bond distances and angles are given in Table 2 and a thermal-ellipsoid representation of the cytidinium cation is shown in Fig. 1. The dimensions of the cation are consistent with those found in other cytidinium salts. The bond distances and angles in the cytosinium moiety are in excellent agreement with the averaged values reported by Taylor & Kennard (1982). In particular, the wide C(2)–N(3)–C(4) angle [ $125.8(3)^\circ$ ] indicates N(3) as the protonation site. The pyrimidine ring is planar ( $\chi^2 12.8$ ) and parallel to *b*, the angle between its normal and the *b* axis being  $0.4(3)^\circ$ . The C(1'), O(2) and N(4) substituents deviate from the pyrimidine best plane by  $0.040(3)$ ,  $0.033(3)$  and  $0.021(4)$  Å, respectively. The exocyclic amino group [C(4)N(4)H<sub>2</sub>] is nearly coplanar with the pyrimidine ring, the dihedral angle being  $5(2)^\circ$ . The conformation of the ribose ring is 2'-*endo* (<sup>2</sup>*E*). In terms of pseudorotation (Altona & Sundaralingam, 1972) the ribose conformation is

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51274 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final fractional coordinates and equivalent isotropic thermal parameters ( $\text{\AA}^2$ )
$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}$
P	0.1936 (1)	0.9418 (1)	0.29750 (5)	0.0251 (3)
O(1P)	0.0335 (3)	0.9097 (4)	0.2878 (1)	0.039 (1)
O(2P)	0.2548 (3)	0.9977 (4)	0.2310 (1)	0.0310 (8)
O(3P)	0.2574 (2)	0.7736 (4)	0.3315 (1)	0.0296 (9)
O(4P)	0.2090 (3)	1.1248 (4)	0.3436 (2)	0.034 (1)
N(1)	0.0041 (3)	0.5757 (4)	0.5794 (1)	0.0222 (9)
C(2)	0.0339 (4)	0.7458 (5)	0.6115 (2)	0.026 (1)
O(2)	0.0164 (3)	0.9012 (4)	0.5871 (1)	0.034 (1)
N(3)	0.0901 (3)	0.7242 (4)	0.6752 (1)	0.026 (1)
C(4)	0.1179 (4)	0.5569 (5)	0.7059 (2)	0.026 (1)
N(4)	0.1732 (4)	0.5564 (6)	0.7662 (2)	0.034 (1)
C(5)	0.0840 (4)	0.3871 (5)	0.6710 (2)	0.027 (1)
C(6)	0.0299 (4)	0.4020 (6)	0.6087 (2)	0.027 (1)
C(1')	-0.0527 (3)	0.5847 (5)	0.5106 (2)	0.024 (1)
C(2')	0.0592 (4)	0.5626 (5)	0.4568 (2)	0.024 (1)
O(2')	0.1289 (3)	0.7370 (4)	0.4491 (1)	0.0312 (9)
C(3')	-0.0256 (4)	0.4894 (5)	0.3975 (2)	0.026 (1)
O(3')	-0.0927 (3)	0.6447 (4)	0.3654 (1)	0.0294 (9)
C(4')	-0.1304 (4)	0.3586 (5)	0.4332 (2)	0.026 (1)
O(4')	-0.1423 (2)	0.4297 (4)	0.5018 (1)	0.0286 (8)
C(5')	-0.0927 (4)	0.1495 (6)	0.4349 (2)	0.035 (1)
O(5')	0.0498 (3)	0.1292 (4)	0.4549 (1)	0.036 (1)

Table 2. Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ )

N(1)—C(2)	1.385 (4)	C(2')—C(3')	1.524 (5)
C(2)—O(2)	1.207 (4)	C(3')—O(3')	1.420 (4)
C(2)—N(3)	1.385 (5)	C(3')—C(4')	1.540 (5)
N(3)—C(4)	1.351 (5)	C(4')—C(5')	1.514 (5)
C(4)—N(4)	1.312 (5)	C(5')—O(5')	1.440 (5)
C(4)—C(5)	1.418 (5)	C(4')—O(4')	1.456 (4)
C(5)—C(6)	1.348 (5)	O(4')—C(1')	1.401 (4)
C(6)—N(1)	1.375 (5)	P—O(1P)	1.574 (3)
N(1)—C(1')	1.474 (4)	P—O(2P)	1.499 (3)
C(1')—C(2')	1.528 (5)	P—O(3P)	1.494 (3)
C(2')—O(2')	1.407 (4)	P—O(4P)	1.586 (3)
C(6)—N(1)—C(2)	122.2 (3)	C(1')—C(2')—O(2')	109.0 (3)
C(6)—N(1)—C(1')	119.9 (3)	O(2')—C(2')—C(3')	117.8 (3)
C(1')—N(1)—C(2)	117.9 (3)	C(2')—C(3')—C(4')	101.4 (3)
N(1)—C(2)—N(3)	114.1 (3)	C(2')—C(3')—O(3')	109.5 (3)
N(1)—C(2)—O(2)	124.5 (3)	O(3')—C(3')—C(4')	111.5 (3)
O(2)—C(2)—N(3)	121.5 (4)	C(3')—C(4')—O(4')	106.2 (3)
C(2)—N(3)—C(4)	125.8 (3)	C(3')—C(4')—C(5')	115.6 (3)
N(3)—C(4)—C(5)	117.7 (3)	O(4')—C(4')—C(5')	109.4 (3)
N(3)—C(4)—N(4)	119.7 (4)	C(4')—C(5')—O(5')	109.4 (3)
N(4)—C(4)—C(5)	122.6 (4)	C(4')—O(4')—C(1')	109.6 (2)
C(4)—C(5)—C(6)	118.3 (4)	O(1P)—P—O(2P)	108.5 (2)
C(5)—C(6)—N(1)	121.9 (4)	O(1P)—P—O(3P)	110.3 (2)
N(1)—C(1')—O(4')	108.2 (3)	O(1P)—P—O(4P)	106.2 (2)
N(1)—C(1')—C(2')	112.5 (3)	O(2P)—P—O(3P)	116.3 (1)
O(4')—C(1')—C(2')	105.6 (3)	O(2P)—P—O(4P)	105.0 (2)
C(1')—C(2')—C(3')	101.3 (3)	O(3P)—P—O(4P)	110.0 (1)

characterized by  $P = 163.9 (8)^\circ$  and  $\tau_m = 40.0 (6)^\circ$ . The same conformation was adopted by the cytidinium cation in the chloride salt [ $P = 162.8 (8)^\circ$ ; Mosset, Bonnet & Galy, 1979] but not in the nitrate salt where it was found to be 3'-endo/2'-exo [ $^3T_2$ ,  $P = 12.7 (7)^\circ$ ; Guy *et al.*, 1976]. The glycosidic torsion angle, which describes the relative orientation of the base with respect to the sugar, is in the *anti* region but has a very

low value [ $34.4 (3)^\circ$ ], quite unusual in 2'-endo ribofuranosides. The torsion angles O(5')—C(5')—C(4')—C(3') ( $\gamma$ ) and O(5')—C(5')—C(4')—O(4') [ $46.6 (4)$  and  $-73.1 (3)^\circ$  respectively] indicate that the side chain assumes the preferred +*gauche* conformation with the C(5')—O(5') bond rotated *ca*  $13^\circ$  from the ideal staggered orientation towards C(4')—C(3').

The P—OH distances in the dihydrogenphosphate anion are significantly longer than the other two P—O bonds (Table 2). The fact that P—O(4P)H is somewhat longer than P—O(1P)H [ $1.586 (3)$  vs  $1.574 (3)$   $\text{\AA}$ ] can be attributed to the hydrogen-bonding situation in this region as O(1)H is only a hydrogen-bond donor while O(4P)H acts as a donor and as an acceptor in two hydrogen bonds (see below). As pointed out by Cruickshank (1961) the sum of the P—O distances in any phosphate is a constant. In the present case this sum equals  $6.153 (6)$   $\text{\AA}$  and is close to the value of  $6.184$   $\text{\AA}$  given by Matheja & Degens (1971). According to Fluck & Maas (1973) the  $\pi$ -bond orders of

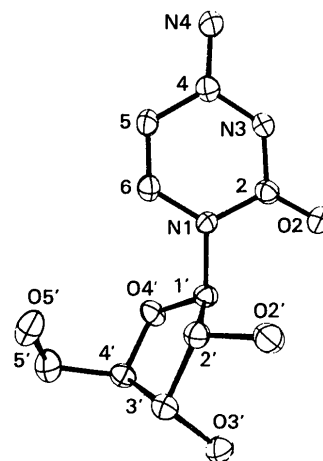


Fig. 1. Thermal-ellipsoid representation of the cytidinium cation drawn at 50% probability level. H atoms have been omitted.

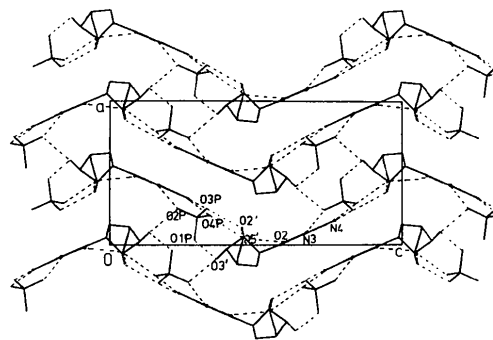
Fig. 2. Projection of the structure down *b*. H atoms have been omitted. O(N)—H...O bonds are indicated by broken lines.

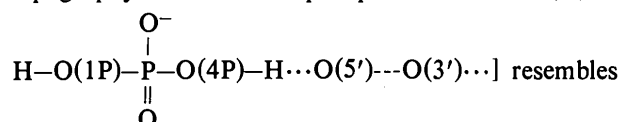
Table 3. *Geometry of the hydrogen bonds*

$D-H \cdots A$	$D-H$ (Å)	$H \cdots A$ (Å)	$D \cdots A$ (Å)	$\angle D-H \cdots A$ (°)
O(1P)—H(1P)···O(3')	0.97 (4)	1.74 (4)	2.706 (4)	175 (2)
O(4P)—H(4P)···O(5')	0.72 (4)	2.02 (4)	2.693 (4)	155 (4)
N(3)—H(3)···O(2P <sup>ii</sup> )	0.91 (4)	1.85 (4)	2.699 (4)	155 (3)
N(4)—H(41)···O(3P <sup>iii</sup> )	0.90 (4)	1.85 (4)	2.739 (5)	170 (3)
N(4)—H(42)···O(4P <sup>iv</sup> )	0.95 (5)	2.02 (4)	2.944 (5)	163 (3)
O(2')—H(2'O)···O(3P)	0.80 (4)	1.87 (4)	2.659 (4)	171 (4)
O(3')—H(3'O)···O(2P <sup>iv</sup> )	0.81 (4)	1.88 (4)	2.681 (4)	170 (3)
O(5')—H(5'O)···O(2'')	0.78 (4)	2.24 (4)	2.861 (4)	137 (4)
O(5')—H(5'O)···O(2')	0.78 (4)	2.47 (5)	3.094 (4)	139 (4)
C(5)—H(5)···O(2P <sup>iii</sup> )	1.08	2.35	3.340 (4)	152

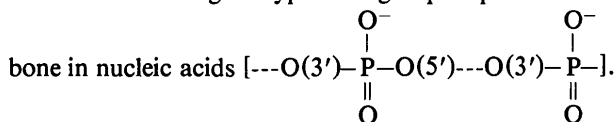
Symmetry codes: (i)  $x, 1+y, z$ ; (ii)  $0.5-x, 2-y, 0.5+z$ ; (iii)  $0.5-x, 1-y, 0.5+z$ ; (iv)  $-x, y-0.5, 0.5-z$ ; (v)  $x, y-1, z$ .

P—O(1P), P—O(2P), P—O(3P) and P—O(4P) are 0.41, 0.64, 0.65 and 0.38 respectively.

All O(N)—H hydrogen-bond donors are utilized in the structure to form a three-dimensional network of quite strong hydrogen bonds illustrated in Fig. 2 and characterized in Table 3. This network shows quite unusual features and deserves a more detailed description. The cation and the corresponding  $xyz$  anion (located at its 'sugar end', Fig. 2) are hydrogen-bonded into an infinite chain running along **b**. This chain is formed with two hydrogen bonds in which the phosphate anion uses both its P—OH donors. It is interesting to observe that the nucleoside units along this chain use their O(3') and O(5') acceptors for hydrogen bonding with the phosphate residues. The topography of the ribose···phosphate chain [...O(3')···



that characterizing a typical sugar-phosphate backbone in nucleic acids



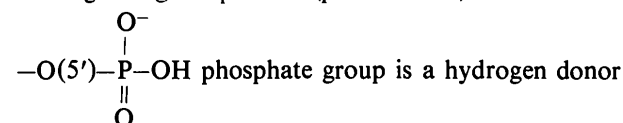
However, due to specific properties of hydrogen bonds as compared to ester PO—C bonds (length, geometry, flexibility), the consecutive nucleoside units are related in the present case by translation along the chain axis (**b** translation). As the cytosinium residue is parallel to **b** (see above) the adjacent nucleobases within the chain are coplanar and 'stacked on edge' (Fig. 2). The  $y$ -screw-related nucleobases are also parallel but show

no overlap. Within the  $\cdots\text{O}(3') \cdots \text{H}-\text{O}(1\text{P})-\text{P}-\text{O}(4\text{P})-\text{H} \cdots \text{O}(5') \cdots \text{O}(3') \cdots$  chain, P—O(1P)H donates a hydrogen bond to O(3') and at the same time O(2')—H on the ribose donates a hydrogen bond to

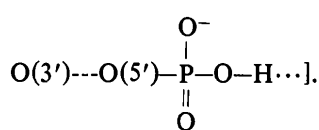
O(3P)—P. Therefore, the ribose on its 3' end is connected to the phosphate *via* two hydrogen bonds. There is also a direct O(5')—H···O(2') link between adjacent sugar residues along the ribose···phosphate chain. In fact, the hydrogen bond at O(5')—H is bifurcated as H(5'O) is accepted by two sites on the same cytidinium cation. The other bond is to the cytosinium carbonyl O(2) atom and is rather weak (Table 3). On its 'base end' the cation also interacts with the anion (at  $0.5-x, 1-y, 0.5+z$ ) forming another hydrogen-bonded chain running along **b**. The base is connected through a pair of N(3)—H···O(2P)P and N(4)—H(42)···O(4P)P hydrogen bonds with one anion and through N(4)—H(41)···O(3P)P with its **b**-translated equivalent.

The total effect of the two hydrogen-bond patterns described above is the existence of pleated sheets consisting of alternating columns of anions and cations running along **b** and linked through hydrogen bonds. The sheets are parallel to (100) and when viewed along **b** have kinks at the glycosidic link (Fig. 2). Three-dimensionality of the hydrogen-bond network is provided by an extra O(3')—H···O(2P)P bond which links neighboring sheets.

It is interesting to note that in the crystal structure of 2'-deoxycytidine 5'-phosphate monohydrate (Viswamitra, Reddy, Lin & Sundaralingam, 1971) there is also an infinite chain of hydrogen-bonded molecules running along a  $2_1$  screw (parallel to **b**) in which the



phosphate group is a hydrogen donor to O(3') of another molecule [...O(5')—P—O—H···



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## Structure of Tetra-*tert*-butylcyclotetraphosphane Monosulfide, (C<sub>4</sub>H<sub>9</sub>P)<sub>4</sub>S

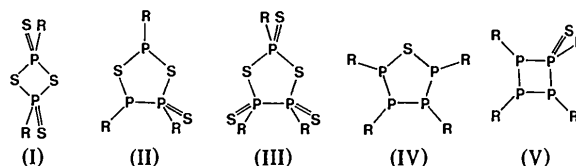
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**Abstract.** C<sub>16</sub>H<sub>36</sub>P<sub>4</sub>S, *M<sub>r</sub>* = 384.3, monoclinic, *P*2<sub>1</sub>/*m*, *a* = 9.542 (2), *b* = 11.324 (2), *c* = 10.518 (4) Å, β = 101.84 (1)°, *V* = 1112 (1) Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 1.15, *D<sub>m</sub>* = 1.16 (1) g cm<sup>-3</sup>, λ(Mo *K*α) = 0.71073 Å, μ = 4.2 cm<sup>-1</sup>, *F*(000) = 416, *T* = 293 K, *R* = 0.030 for 1399 reflections with *F<sub>o</sub>*<sup>2</sup> > 3σ(*F<sub>o</sub>*<sup>2</sup>). The molecule has a non-planar ring of four P atoms; each is bonded to one *tert*-butyl group and one is bonded to an exocyclic S atom. The P–P distances are 2.214 (1) to 2.222 (1) Å, the P–P–P angles range from 86.46 (2) to 90.17 (2)°, and the P–P–P–P torsion angles average 20.05 (5)°. The P–C distances average 1.885 (5) Å and the P=S distance is 1.954 (1) Å.

**Introduction.** Four different stoichiometries are well established for molecules composed of sulfur and organophosphorus (P–R, R = aryl or alkyl) moieties: (PR)<sub>2</sub>S<sub>4</sub> (I), (PR)<sub>3</sub>S<sub>3</sub> (II), (PR)<sub>3</sub>S<sub>5</sub> (III), and (PR)<sub>4</sub>S (IV) or (V). As shown, these molecules have been found to be cyclic with either four- or five-membered rings.



The four-membered-ring structure shown for (I) has been verified by X-ray structure determinations of the methyl (Wheatley, 1962; Daly, 1964) and *tert*-butyl (Shore, Pennington, Noble & Cordes, 1988) molecules. The (PR)<sub>3</sub>S<sub>3</sub> molecule was first reported as a tetramer (Maier, 1963); the asymmetric structure (II) of R<sub>3</sub>P<sub>3</sub>S<sub>3</sub> (R = aryl) rather than the initially assumed six-membered P<sub>3</sub>S<sub>3</sub> ring is the conclusion of two independent NMR studies (LeGeyt & Paddock, 1975; Baudler, Koch, Vakraatsas, Tolls & Kipker, 1975). The (PR)<sub>3</sub>S<sub>5</sub> stoichiometry has only been reported (Burg & Parker, 1970) for R = CF<sub>3</sub>; structure (III) is proposed on the basis of NMR spectral analysis. Structure (V) was