# P₆S₅(C₄H₉)₂, the First Organophosphorus Chalcogen Molecule with a Brexane Skeleton

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## Abstract

$P_6S_5(C_4H_9)_2$, 5,8-di-*tert*-butyl-5,8-dithioxo-2,4,9-trithia-1$\lambda^3$,3$\lambda^3$,5$\lambda^5$,6$\lambda^3$,7$\lambda^3$,8$\lambda^5$-hexaphosphatricyclo-[4.3.0.0$^{3,7}$]nonane, $M_r = 460.40$, monoclinic, $P2_1/c$, $a = 12.255$ (17), $b = 12.866$ (14), $c = 12.522$ (12) Å, $\beta = 100.53$ (9)°, $V = 1941$ (4) Å$^3$, $Z = 4$, $D_x = 1.575$ Mg m$^{-3}$, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 1.048$ mm$^{-1}$, $F(000) = 944$, $T = 295$ K, $R = 0.042$ for 2226 observed unique reflections. The molecule is the first P–S analogue of the tricyclic brexane. It is formally obtained from a norbornane-structured $P_5S_2$ by addition of a PS bridge. The bond angles and distances [for P—P 2.180 (2)–2.217 (2) Å, for endocyclic P—S 2.112 (2)–2.136 (2) Å, for exocyclic P—S 1.936 (3) and 1.941 (3) Å, and for P—C 1.846 (6) and 1.851 (6) Å] agree well with those of similar compounds. $P_6S_5(C_4H_9)_2$ is one of several products, obtained from reaction of $P_4S_3$ with *tert*-butyl iodide in $CS_2$. Single crystals were obtained by fractional crystallization.

## Introduction

$P_4S_3$ has a molecular structure which contains an approximate tetrahedron of P atoms, and which is formed from a triangular $P_3$ base connected by three chalcogen bridges to the apical fourth P atom. The addition of halogens or pseudohalogens to one P—P bond of the $P_3$ base leads to the $\alpha$- and $\beta$-$P_4E_3X(Y)$ series ($E = S$, Se; $X$ and $Y$ are halogen or pseudohalogen) (Penney & Sheldrick, 1970; Blachnik, Kurz & Wickel, 1984; Tattershall, 1987). We have tried to react $P_4S_3$ with alkyl iodides in order to get compounds of the type $\alpha$- and $\beta$-$P_4S_3IR$. During this investigation the formation of $P_6S_5(C_4H_9)_2$ was observed. Crystal structure analysis was performed in order to confirm that the structure of the molecule is that suggested by $^{31}$P NMR spectroscopy. The X-ray structure shows that the title compound is a P–S analogue of brexane.

## Experimental

$P_4S_3$ was dissolved, together with *tert*-butyl iodide, in $CS_2$ and exposed to light for a period of one month. After this treatment the solution was filtered to separate it from polymeric products and then cooled to 243 K. The raw product which crystallized from this solution contained [C₄H₉(S)PS]₂, $P_4S_3$ and $P_6S_5(C_4H_9)_2$. To remove $P_4S_3$ and [C₄H₉(S)PS]₂ it was washed with THF and the residue dissolved in $CS_2$. On cooling colourless single crystals of $P_6S_5(C_4H_9)_2$ were obtained. The compound is stable to both moisture and air, but decomposes above 473 K. A nearly cubic crystal of 0.45 mm diameter was mounted in a sealed glass capillary on an Enraf–Nonius CAD-4 diffractometer. Orientation matrix and cell parameters were determined from centring of 25 reflections with $18 \le 2\theta \le 26°$. The intensities of 3409 unique reflections in the range $2 \le 2\theta \le 50°$, $-14 \le h \le 14$, $0 \le k \le 15$, $0 \le l \le 15$ were collected by $\omega$–$2\theta$ scans with graphite-monochromatized Mo $K\alpha$ radiation. Intensities were corrected for Lorentz and polarization effects. Absorption corrections were applied using the program *DIFABS* (Walker & Stuart, 1983). Intensity variations of the standard reflections 044, 460 and 454 were not observed. 955 reflections with $I < 2\sigma_I$ ($\sigma_I$ from counting statistics) were considered as unobserved.

The P and S positions were obtained from a direct methods $E$ map using *MULTAN*11/82 (Main *et al.*, 1982), the C positions from subsequent $\Delta F$ syntheses and least-squares refinements. The 18 H-atom positions could also be determined from $\Delta F$ syntheses, indicating a staggered conformation of the *tert*-butyl groups, but six of them could not be refined properly, *i.e.* were shifted towards neighbouring P and S atoms. Therefore, and for a better interpretation of possible H contacts, all H atoms were included in structure-factor calculations with ideal tetrahedral positions and isotropic thermal parameters of the bonded C atoms, but not refined. Subse-

Table 1. *Atomic coordinates and equivalent isotropic displacement parameters ($\text{Å}^2$) for the non-H atoms with e.s.d.'s in parentheses*

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

| | x | y | z | $B_{eq}$ |
|---|---|---|---|---|
| S1 | 0.1636 (1) | 0.2011 (1) | 0.1764 (1) | 3.13 (3) |
| S2 | 0.4914 (1) | 0.1575 (1) | 0.5449 (1) | 3.29 (4) |
| S3 | 0.0401 (2) | 0.1888 (1) | 0.4013 (1) | 4.01 (4) |
| S4 | 0.5937 (2) | 0.0876 (1) | 0.3184 (1) | 4.40 (4) |
| S5 | 0.3013 (2) | 0.0399 (1) | 0.3610 (1) | 3.44 (4) |
| P1 | 0.3215 (1) | 0.1319 (1) | 0.2263 (1) | 3.04 (4) |
| P2 | 0.3977 (1) | 0.2768 (1) | 0.2983 (1) | 2.49 (3) |
| P3 | 0.5439 (1) | 0.2012 (1) | 0.3988 (1) | 2.68 (3) |
| P4 | 0.3177 (1) | 0.1399 (1) | 0.4969 (1) | 2.84 (4) |
| P5 | 0.2975 (1) | 0.2965 (1) | 0.4239 (1) | 2.35 (3) |
| P6 | 0.1317 (1) | 0.2711 (1) | 0.3223 (1) | 2.45 (3) |
| C1 | 0.0761 (5) | 0.4007 (5) | 0.2785 (5) | 2.9 (1) |
| C2 | 0.0469 (6) | 0.4557 (5) | 0.3789 (5) | 4.7 (2) |
| C3 | −0.0307 (5) | 0.3840 (6) | 0.1934 (5) | 4.9 (2) |
| C4 | 0.1611 (5) | 0.4639 (5) | 0.2308 (5) | 4.1 (2) |
| C5 | 0.6484 (5) | 0.3040 (5) | 0.4412 (5) | 3.2 (1) |
| C6 | 0.5951 (6) | 0.3963 (5) | 0.4876 (6) | 4.9 (2) |
| C7 | 0.7416 (6) | 0.2551 (6) | 0.5269 (6) | 5.7 (2) |
| C8 | 0.6968 (5) | 0.3348 (6) | 0.3433 (5) | 4.6 (2) |

quent full-matrix least-squares refinements of the scale factor and 171 positional and anisotropic thermal parameters of P, S and C with tetrahedrally generated H positions based on 2226 $F$ magnitudes with $F \geq 2\sigma_F$ converged without any shift at a final $R = 0.042$ ($wR = 0.036$, $w = 1/\sigma_I$, $S = 2.57$). Peaks in the final $\Delta F$ map were within $\pm 0.42$ (9) e $\text{Å}^{-3}$. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Calculations were performed with the *SDP* package (B. A. Frenz & Associates Inc., 1985) on a DEC computer VAX 8820. Final atomic parameters are given in Table 1, bond lengths and angles, some contact distances and selected torsion angles in Table 2.*

## Discussion

A view of the molecule is shown in Fig. 1. Distances and angles within the *tert*-butyl groups are found to be normal. The molecule has the point symmetry 1 ($C_1$). The X-ray structure analysis confirms that the molecule is 5,8-di-*tert*-butyl-5,8-dithioxo-2,4,9-trithiahexaphosphatricyclo[4.3.0.0$^{3,7}$]nonane.

The skeleton of the molecule, which is the first P–S analogue of the tricyclic brexane (Nickon, Kwasnik, Swartz, Williams & DiGiorgio, 1965), is formally derived from a norbornane-structured $P_5S_2$ unit by the addition of a PS bridge. The $P_5S_2$ part of the molecule consists of two nearly regular five-

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Table 2. *Selected bond distances ($\text{Å}$), angles (°), intramolecular contact distances ($\text{Å}$) and torsion angles (°) with e.s.d.'s in parentheses*

| | | | |
|---|---|---|---|
| S1—P1 | 2.117 (2) | P3—C5 | 1.851 (6) |
| S1—P6 | 2.136 (2) | P4—P5 | 2.208 (2) |
| S2—P3 | 2.123 (2) | P5—P6 | 2.216 (2) |
| S2—P4 | 2.116 (2) | P6—C1 | 1.846 (6) |
| S3—P6 | 1.941 (3) | C1—C2 | 1.542 (9) |
| S4—P3 | 1.936 (3) | C1—C3 | 1.543 (8) |
| S5—P1 | 2.112 (2) | C1—C4 | 1.527 (9) |
| S5—P4 | 2.113 (2) | C5—C6 | 1.520 (9) |
| P1—P2 | 2.203 (2) | C5—C7 | 1.551 (8) |
| P2—P3 | 2.217 (2) | C5—C8 | 1.509 (9) |
| P2—P5 | 2.180 (2) | | |
| | | | |
| H32···S1 | 2.78 (7)* | H63···S2 | 2.87 (7)* |
| H42···P5 | 2.83 (7)* | H72···S2 | 2.75 (7)* |
| H43···S1 | 2.87 (7)* | H82···P3 | 2.89 (7)* |
| H62···P2 | 2.82 (7)* | H83···P3 | 2.89 (7)* |
| | | | |
| P1—S1—P6 | 103.02 (8) | S4—P3—C5 | 114.9 (2) |
| P3—S2—P4 | 103.34 (8) | P2—P3—C5 | 107.1 (2) |
| P1—S5—P4 | 107.1 (1) | S2—P4—S5 | 103.7 (1) |
| S1—P1—S5 | 103.7 (1) | S2—P4—P5 | 92.90 (9) |
| S1—P1—P2 | 93.52 (9) | S5—P4—P5 | 103.60 (8) |
| S5—P1—P2 | 104.47 (9) | P2—P5—P4 | 99.04 (9) |
| P1—P2—P3 | 95.70 (9) | P2—P5—P6 | 98.44 (8) |
| P1—P2—P5 | 98.13 (9) | P4—P5—P6 | 97.15 (8) |
| P3—P2—P5 | 98.32 (8) | S1—P6—S3 | 114.8 (1) |
| S2—P3—S4 | 115.0 (1) | S1—P6—P5 | 105.14 (9) |
| S2—P3—P2 | 105.37 (9) | S1—P6—C1 | 104.0 (2) |
| S2—P3—C5 | 104.2 (2) | S3—P6—P5 | 110.05 (9) |
| S4—P3—P2 | 109.57 (9) | S3—P6—C1 | 115.3 (2) |
| | | P5—P6—C1 | 106.7 (2) |
| | | | |
| P6—S1—P1—S5 | 53.2 (1) | S5—P1—P2—P5 | −42.2 (1) |
| P6—S1—P1—P2 | −52.6 (1) | P1—P2—P3—S2 | −85.8 (1) |
| P1—S1—P6—P5 | 24.1 (1) | P5—P2—P3—S2 | 13.3 (1) |
| P4—S2—P3—P2 | 26.1 (1) | P1—P2—P5—P4 | 50.8 (1) |
| P3—S2—P4—S5 | 51.5 (1) | P1—P2—P5—P6 | −47.9 (1) |
| P3—S2—P4—P5 | −53.2 (1) | P3—P2—P5—P4 | −46.2 (1) |
| P4—S5—P1—S1 | −81.3 (1) | P3—P2—P5—P6 | −144.9 (1) |
| P4—S5—P1—P2 | 16.1 (1) | S2—P6—P5—P2 | 62.2 (1) |
| P1—S5—P4—S2 | −80.0 (1) | S2—P4—P5—P6 | 161.9 (1) |
| P1—S5—P4—P5 | 16.5 (1) | S5—P4—P5—P2 | −42.7 (1) |
| S1—P1—P2—P3 | 162.2 (1) | S5—P4—P5—P6 | 57.1 (1) |
| S1—P1—P2—P5 | 62.9 (1) | P2—P5—P6—S1 | 15.6 (1) |
| S5—P1—P2—P3 | 57.1 (1) | P4—P5—P6—S1 | −84.8 (1) |

\* From tetrahedrally generated H atoms at 1.096 Å distance; e.s.d.'s are from refinement with H atoms included.

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membered rings. By the addition of the PS bridge a new five-membered ring is formed. The P atom in the external bridge and the opposite P atom in the (PS) bridge of the norbornane each bear an additional *tert*-butyl group and an *exo*-S atom. Polycyclic phosphorus compounds of the same type as the molecular compounds $P_5(CH_2)_4R$ ($R = $ Me, Et) (Baudler & Esat, 1983) and *b*-$P_9R_5$ (Baudler & Arndt, 1984) have already been reported. $P_9$ units related to this class of molecules are condensed to form helical $P_7$ chains in the compounds LiP$_7$ and NaP$_7$ (von Schnering & Wichelhaus, 1972). $P_6S_5(C_4H_9)_2$ is a further example of the structural similarity of twofold covalently bonded P$^-$ ions and S atoms.

Four P—P bond distances are found in the range 2.203 (2)–2.217 (2) Å, which correspond to single-

bond distances of phosphorus in strained structures [$d_{P—P}(P_4)$] = 2.209 (5) Å, Simon, Borrman & Craubner (1987); $d_{P—P}$(P-violet) = 2.219 (3) Å, Thurn & Krebs (1969)]. The largest values [P2—P3 2.217 (2), P5—P6 2.216 (2) Å] are observed in the neighbourhood of the substituted P atoms, due to the steric influence of the large *tert*-butyl ligands. The shortest distance [P2—P5 2.180(2) Å] is observed between those P atoms which have only phosphorus neighbours. The P—S bond distances in the molecular skeleton correspond, within the limits of error, to the values 2.09–2.14 Å for endocyclic P—S bonds in $P_4S_n$ molecules (Corbridge, 1974). The exocyclic P—S double-bond distances of 1.936 (3) and 1.941 (3) Å agree with the respective distances which are observed in $P_4S_n$ compounds with *exo*-S atoms. The mean P—C distance [1.849 (6) Å] is considerably shorter than in the related 5,8,9-tri-*tert*-butyltetracyclo[4.3.0.0$^{2,4}$.0$^{3,7}$]nonaphosphane (Tebbe & Fehér, 1987). All bond angles in the phosphorus–sulfur skeleton of the molecule are in accordance with those observed in other phosphorus chal-

cogenides [P$^{III}$—S—P$^{V}$ 103° in $P_4S_7$, P$^{III}$—S—P$^{III}$ 104° in $P_4S_5$, S—P$^{V}$—S ~110° in $P_4S_7$, P—P—P 100° in (*PR*)$_5$, Corbridge (1974)]. The P—P—P bond angles scatter only slightly around a mean value of 98.1°, which is smaller than expected for a $\psi$-tetrahedral configuration. The two endocyclic S—P—S bond angles, *i.e.* S1—P1—S5 and S2—P4—S5, are identical [103.7 (1)°] and again smaller than expected for a $\psi$-tetrahedron. The S—P—P bond angles of the $\lambda^3$P atoms, *i.e.* P1, P2, P4, P5, have a mean value of 98.6° which is smaller than that at the $\lambda^5$P atoms P3 and P6 *viz.* 107.5°. The molecular arrangement in the crystal is shown in Fig. 2. Intermolecular contact distances are at least within the range of the sum of the van der Waals radii. This means that bond distances and angles are free from the effects of molecular packing. However, intramolecular interactions are strong, especially some of the H—P and H—S contact distances (see Table 2), and are considerably shorter than the van der Waals distances. These interactions cause the P—S bridges to twist [$\tau$(P1—S1—P6—P5) = 24.05°, $\tau$(P4—S2—P3—P2) = 26.15°] to an extent which is comparable with the dihedral angle of a similar bridge in 5,8,9-tri-*tert*-butyltetracyclononaphosphane ($\tau$ = 22.61°). Also, the other dihedral and torsion angles (see Table 2) related to the exocyclic S and *tert*-butyl ligands are similar for comparable parts of the skeleton.
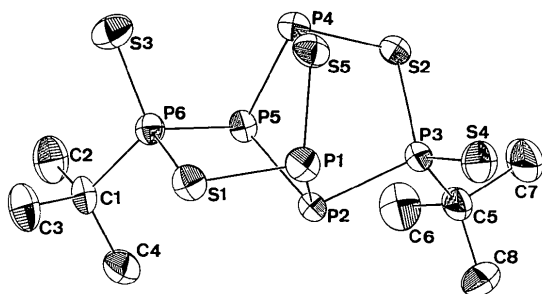
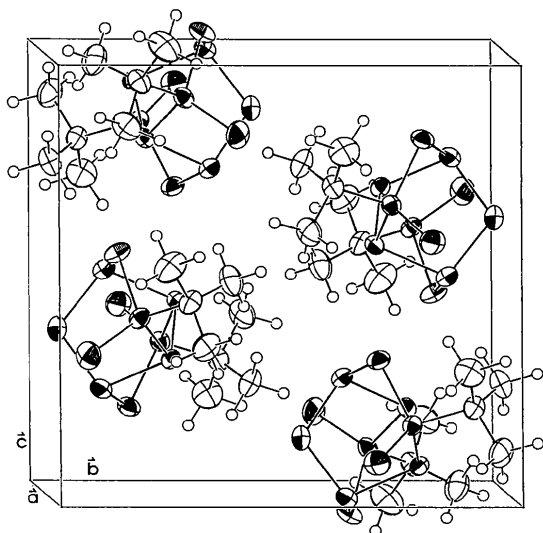Fig. 1. Structure of the molecule excluding H atoms and with thermal ellipsoids shown at 50% probability.



Fig. 2. Stereo representation of the crystal structure viewed along [100].

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