

A new polymorph of 2,2,4,4,6,6-hexaisothiocyanatocyclotriphosphazene

Elmar Kessenich, Axel Schulz*
and Kurt PolbornDepartment of Chemistry, Ludwig-Maximilians-
University, Butenandtstrasse 5-13 (D), D-81377
Munich, GermanyCorrespondence e-mail:
lex@cup.uni-muenchen.de

Key indicators

Single-crystal X-ray study

T = 293 K

Mean $\sigma(\text{N}-\text{C}) = 0.009 \text{ \AA}$

R factor = 0.055

wR factor = 0.131

Data-to-parameter ratio = 13.4

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

A new polymorph of the title compound, $\text{C}_6\text{N}_9\text{P}_3\text{S}_6$, has been found. In contrast to the already known polymorph, which crystallizes with $Z' = 1$ in $P\bar{1}$, the title structure crystallizes in $P2_1/c$ with $Z' = 2$. The two independent molecules in the asymmetric unit show large differences in the ring structure. The non-planarity of the phosphazene ring indicates weak $\text{S} \cdots \text{S}$ interactions of the isothiocyanate groups, as well as packing effects.

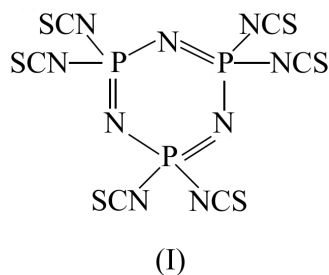
Received 2 October 2001

Accepted 7 December 2001

Online 11 January 2002

Comment

2,2,4,4,6,6-Hexaisothiocyanatocyclotriphosphazene, (I), was first structurally characterized by Faught *et al.* (1970). In contrast to the known structure, we report here a new polymorph with two molecules in the asymmetric unit.



Whereas one of the molecules is similar to the already known structure, the other molecule shows a non-planar phosphazene ring, with one P atom 0.313 \AA from the plane of the remaining five atoms (Fig. 1). This phosphazene ring system adopts a slightly distorted half-chair conformation. The P–N ring distances vary from $1.56(1)$ to $1.58(2) \text{ \AA}$ and the average P–N distance in the ring is 1.568 \AA , compared with 1.58 \AA reported by Faught *et al.* (1970). The reasons for the non-planar ring could be packing effects and the short intermolecular $\text{S} \cdots \text{S}$ contacts (*ca.* 3.74 \AA). Because of the non-aromaticity of cyclic phosphazene rings, they do not have to be planar. The bond situation can be best described with the Dewar–Isle model (Dewar *et al.*, 1960), where the π -system is interrupted by sign change of the π orbitals at the P atoms. The N8/C5/S5 isothiocyanato group connected to P3 is nearly parallel to the ring, whereas the other isothiocyanato groups occupy axial positions with respect to the phosphazene ring (Fig. 2). The phosphazene ring of the second molecule in the asymmetric unit is nearly planar and the isothiocyanate groups are all in axial positions (Fig. 2). The P–N(isothiocyanate) bonds vary from 1.626 to 1.652 \AA , indicating a bond order between one and two. A typical single P–N bond is found in 6-oxo-2,2,4,4,6,6-pentaphenoxycyclotri- λ 5-phosphazane-1,3-diene of $1.683(1) \text{ \AA}$ (Parvez *et al.*, 1991) or in NaPO_3NH_3 of

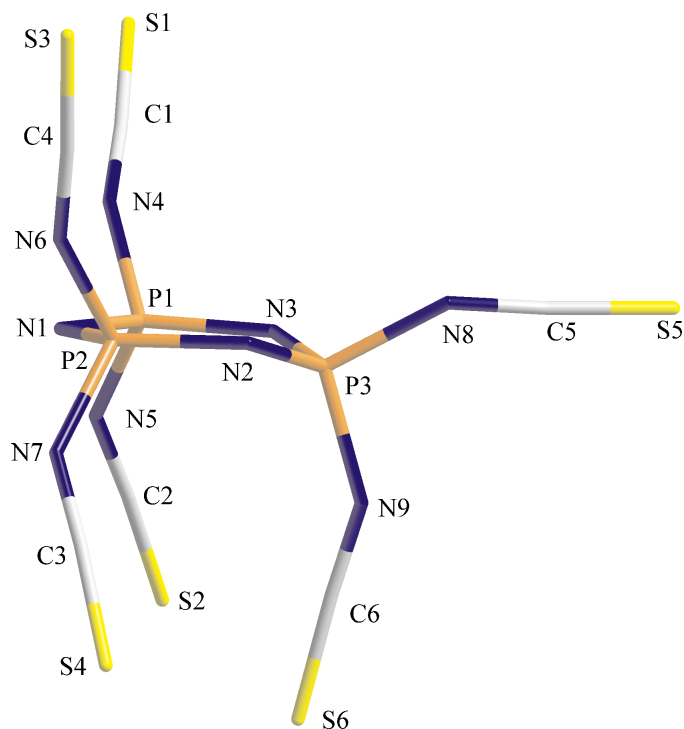


Figure 1
View of one molecule of the title compound in the asymmetric unit.

1.77 (2) Å (Cruickshank, 1964). The average N—C—S angle is $176.7 \pm 1.5^\circ$, compared with the reported angle of 175° (Parvez *et al.*, 1991).

Experimental

2,2,4,4,6,6-Hexaisothiocyanatocyclotriphosphazene was prepared by the reaction of 2,2,4,4,6,6-hexachlorocyclotriphosphazene (0.425 g, 0.76 mmol) in 10 ml acetone and potassium thiocyanate (1.00 g, 10.3 mmol) in 40 ml acetone. To the solution, 18-crown-6 ether (0.2 g, 0.76 mmol) was added and the mixture refluxed for 30 min. The residue was filtered off and the solution cooled in a dry-ice bath. The solid which formed was collected and recrystallized from *n*-heptane to give 0.534 g (1.5 mmol, 85%) of 2,2,4,4,6,6-hexaisothiocyanatocyclotriphosphazene.

Crystal data

$C_6N_9P_3S_6$
 $M_r = 483.42$
 Monoclinic, $P2_1/c$
 $a = 7.977$ (2) Å
 $b = 34.551$ (8) Å
 $c = 13.691$ (3) Å
 $\beta = 101.98$ (2)°
 $V = 3691.1$ (14) Å³
 $Z = 8$

$D_x = 1.740$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 9\text{--}16^\circ$
 $\mu = 1.01$ mm⁻¹
 $T = 293$ (2) K
 Plate, colourless
 $0.53 \times 0.43 \times 0.33$ mm

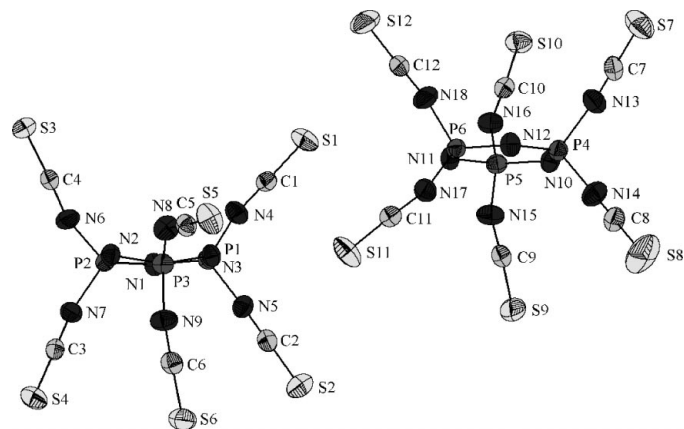


Figure 2
The molecular structure showing 50% probability displacement ellipsoids.

Data collection

Nonius MACH3 diffractometer
 ω scans
 Absorption correction: empirical ψ scan
 $T_{\min} = 0.949$, $T_{\max} = 0.999$
 6069 measured reflections
 5810 independent reflections
 4208 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.014$
 $\theta_{\max} = 24.0^\circ$
 $h = -8 \rightarrow 9$
 $k = 0 \rightarrow 39$
 $l = -15 \rightarrow 0$
 3 standard reflections
 frequency: 7200 min
 intensity decay: -0.1%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.055$
 $wR(F^2) = 0.131$
 $S = 1.13$
 5810 reflections
 433 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0542P)^2 + 7.7164P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.017$
 $\Delta\rho_{\max} = 0.41$ e Å⁻³
 $\Delta\rho_{\min} = -0.37$ e Å⁻³

Data collection: *MACH3 Software* (Nonius, 1977); cell refinement: *MACH3 Software*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993); molecular graphics: *ZORTEP* (Zsolnai, 1994); software used to prepare material for publication: *SHELXL93*.

References

- Parvez, M., Sukky, K. & Allcock, H. R. (1991). *Acta Cryst.* **C47**, 466–468.
 Cruickshank, D. W. J. (1964). *Acta Cryst.* **17**, 671–672.
 Dewar, M. J. S., Lucken, E. A. C. & Whitehead, M. A. J. (1960). *J. Chem. Soc.* pp. 2423–2439.
 Fair, C. K. (1990). *MolEN*. Enraf–Nonius, Delft, The Netherlands.
 Faught, J. B., Moeller, T. & Paul, I. C. (1970). *Inorg. Chem.* **9**, 1656–1659.
 Nonius (1997). *MACH3 Software*. Nonius BV, Delft, The Netherlands.
 Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
 Sheldrick, G. M. (1993). *SHELXL93*. University of Göttingen, Germany.
 Zsolnai, L. (1994). *ZORTEP*. University of Heidelberg, Germany.