

Structure of *cis*-5,5-Dichloro-1,3-diphenyl-1 λ^6 ,3 λ^6 ,2,4,6,5 λ^5 -dithiatriazaphosphorine 1,3-Dioxide

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Abstract. C₁₂H₁₀Cl₂N₃O₂PS₂, $M_r = 394.22$, triclinic, $P\bar{1}$, $a = 9.8757$ (4), $b = 9.9319$ (4), $c = 17.219$ (1) Å, $\alpha = 96.183$ (4), $\beta = 96.283$ (4), $\gamma = 76.525$ (3)°, $V = 1626.6$ (1) Å³, $Z = 4$, $D_x = 1.610$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 7.5$ cm⁻¹, $F(000) = 800$, $T = 295$ K, $R = 0.042$ for 4018 observed reflections. The unit cell contains two independent molecules, both with a skew-boat conformation of the inorganic ring. Phenyl substituents are in *cis* positions. Mean bond lengths are N–P = 1.573 (3), N–S = 1.575 (3), S–O = 1.428 (1), S–C = 1.761 (2), P–Cl = 1.981 (2) and C–C = 1.374 (2) Å. The average endocyclic angles at P and S are 118.4 (2) and 112.3 (1)° respectively. The endocyclic angles at N range from 121.2 (2) to 122.6 (2)°.

Introduction. From the molecular structures of *cis*-NPCl₂(NSOF)₂ (Tucker & van de Grampsel, 1974) and *cis*-NPCl₂(NSOCl)₂ (van de Grampsel & Vos, 1969) it can be concluded that the sulfur-bonded substituents influence the charge distribution over the ring; the higher the electronegativity of the sulfur center the smaller the N–S(O,X) bond length and the larger the N–P bond length. The electron-withdrawing capacity of the sulfur center is also reflected by a high-field shift of the ³¹P resonance signal (X=F, $\delta^{31}\text{P} = 30.9$; X=Cl, $\delta^{31}\text{P} = 27.6$). Besides the aforementioned compounds of which also the *trans* isomers are known (van de Grampsel, 1981), two other related compounds have been prepared, *viz.* *cis*-NPCl₂(NSOPh)₂ ($\delta^{31}\text{P} = 25.4$) and *trans*-NPCl₂(NSOPh)₂ ($\delta^{31}\text{P} = 22.1$) (van den Berg, de Ruiter & van de Grampsel, 1976), the crystal structure of the latter having been determined (van Bolhuis, van den Berg & van de Grampsel, 1981). The crystal-structure determination of the title compound

was undertaken in order to confirm its structure assignment based on NMR data and to investigate the influence of the SOPh group on the electron distribution over the inorganic ring skeleton.

Experimental. Suitable crystals obtained by recrystallization from diethyl ether. Enraf–Nonius CAD-4F diffractometer, graphite-monochromated Mo $K\alpha$ radiation; colorless crystal 0.125 × 0.25 × 0.40 mm glued on top of a glass fiber; accurate cell parameters calculated from setting angles of 22 reflections ($20.0 < \theta < 21.8^\circ$) in four alternative settings (de Boer & Duisenberg, 1984). The cell was checked for the presence of higher lattice symmetry (Le Page, 1982); the observed pseudo mC lattice was found to be inconsistent with the symmetry of the reflection data. 5739 reflections ($h\ 0 \rightarrow 11$, $k\ -11 \rightarrow 11$, $l\ -20 \rightarrow 20$); $1.2 < \theta < 25^\circ$; $\omega/2\theta$ scan; $\Delta\omega = (0.70 + 0.35 \text{tg}\theta)^\circ$. Three reference reflections measured every 2 h (121: r.m.s.d. 0.5%; 104: r.m.s.d. 1.4%; 321: r.m.s.d. 0.6%) showed a small linear decay of 1% during the 60.5 h of X-ray exposure time. A 360° ψ scan for the reflection 426 showed an intensity variation up to 3.5% about the mean. Intensities corrected for Lorentz and polarization effects and the small decay, not for absorption. Variance $\sigma^2(I)$ calculated based on counting statistics plus a term $(PI)^2$ where $P (=0.010)$ is the instability constant (McCandlish, Stout & Andrews, 1975). Structure solved by direct methods using GENTAN (Stewart & Hall, 1983), refined on F by block-diagonal least-squares techniques with anisotropic thermal parameters for non-H atoms. H atoms located in difference Fourier map, included in final refinement with one overall isotropic temperature factor. Convergence reached at $R = 0.042$, $wR = 0.034$; $w = 1/\sigma^2(F)$; $S = 1.546$; 4018 observed reflections with

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$I > 2.5\sigma(I)$; 458 refined parameters; maximum $\Delta/\sigma = 0.67$. Minimum and maximum residual densities in final difference Fourier map -0.42 and $0.32 \text{ e } \text{Å}^{-3}$. The final values of the refined parameters are given in Table 1.* Scattering factors from Cromer & Mann (1968). Anomalous dispersion from Cromer & Liberman (1970). Calculations carried out on the Cyber 180-855 of the University of Utrecht Computer Center with program packages *XTAL* (Stewart & Hall, 1983) and *EUCLID* (Spek, 1982; calculation of geometric data and preparation of illustrations including an extended version of the program *PLUTO*).

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond lengths and angles involving H and *ORTEP* plots (Johnson, 1965) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42592 (34 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final atomic coordinates and equivalent isotropic thermal parameters and their *e.s.d.*'s in parentheses

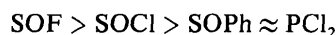
	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}^*(\text{Å}^2)$
Molecule A				
Cl(11)	0.2113 (1)	0.3410 (1)	0.29818 (7)	0.0857 (5)
Cl(12)	0.0306 (1)	0.6287 (1)	0.26635 (7)	0.0981 (5)
S(11)	0.2575 (1)	0.43112 (9)	0.07574 (5)	0.0431 (3)
S(12)	0.4252 (1)	0.5629 (1)	0.18284 (6)	0.0477 (3)
P(11)	0.1957 (1)	0.4928 (1)	0.22922 (6)	0.0543 (4)
O(11)	0.2795 (3)	0.3015 (2)	0.0285 (1)	0.061 (1)
O(12)	0.5690 (3)	0.5358 (3)	0.2120 (2)	0.069 (1)
N(11)	0.1587 (3)	0.4385 (3)	0.1415 (2)	0.052 (1)
N(12)	0.4053 (3)	0.4578 (3)	0.1092 (2)	0.041 (1)
N(13)	0.3271 (3)	0.5578 (3)	0.2483 (2)	0.059 (1)
C(11)	0.1753 (3)	0.5641 (3)	0.0152 (2)	0.039 (1)
C(12)	0.2174 (4)	0.5518 (4)	-0.0595 (2)	0.055 (2)
C(13)	0.1655 (4)	0.6627 (5)	-0.1054 (2)	0.072 (2)
C(14)	0.0767 (4)	0.7788 (4)	-0.0776 (2)	0.071 (2)
C(15)	0.0340 (4)	0.7896 (4)	-0.0033 (2)	0.063 (2)
C(16)	0.0836 (4)	0.6812 (4)	0.0435 (2)	0.049 (1)
C(17)	0.3763 (4)	0.7319 (3)	0.1511 (2)	0.040 (1)
C(18)	0.2952 (4)	0.8385 (4)	0.1942 (2)	0.057 (2)
C(19)	0.2600 (4)	0.9691 (4)	0.1664 (2)	0.072 (2)
C(110)	0.3045 (4)	0.9898 (4)	0.0974 (2)	0.070 (2)
C(111)	0.3842 (4)	0.8826 (4)	0.0541 (2)	0.066 (2)
C(112)	0.4217 (4)	0.7524 (4)	0.0806 (2)	0.052 (1)
Molecule B				
Cl(21)	0.7463 (1)	0.8732 (1)	0.13339 (6)	0.0717 (4)
Cl(22)	0.5761 (1)	1.1654 (1)	0.18067 (6)	0.0708 (4)
S(21)	0.7423 (1)	0.93122 (9)	0.37418 (6)	0.0496 (3)
S(22)	0.9402 (1)	1.05827 (9)	0.32942 (5)	0.0435 (3)
P(21)	0.7216 (1)	1.0134 (1)	0.22478 (6)	0.0461 (4)
O(21)	0.7466 (3)	0.7974 (2)	0.3989 (2)	0.075 (1)
O(22)	1.0882 (2)	1.0246 (3)	0.3268 (1)	0.062 (1)
N(21)	0.6603 (3)	0.9562 (3)	0.2920 (2)	0.054 (1)
N(22)	0.8979 (3)	0.9494 (3)	0.3773 (2)	0.044 (1)
N(23)	0.8603 (3)	1.0664 (3)	0.2452 (2)	0.048 (1)
C(21)	0.6546 (4)	1.0602 (4)	0.4404 (2)	0.048 (1)
C(22)	0.6811 (4)	1.0385 (5)	0.5187 (2)	0.076 (2)
C(23)	0.6233 (5)	1.1435 (6)	0.5731 (2)	0.097 (2)
C(24)	0.5452 (5)	1.2639 (5)	0.5491 (3)	0.096 (2)
C(25)	0.5173 (4)	1.2856 (4)	0.4722 (3)	0.083 (2)
C(26)	0.5719 (4)	1.1827 (4)	0.4164 (2)	0.063 (2)
C(27)	0.8914 (3)	1.2238 (3)	0.3798 (2)	0.038 (1)
C(28)	0.8198 (4)	1.3371 (4)	0.3407 (2)	0.052 (1)
C(29)	0.7857 (4)	1.4644 (4)	0.3819 (2)	0.062 (2)
C(210)	0.8216 (4)	1.4799 (4)	0.4602 (2)	0.067 (2)
C(211)	0.8919 (4)	1.3663 (4)	0.4990 (2)	0.068 (2)
C(212)	0.9285 (4)	1.2368 (4)	0.4590 (2)	0.053 (1)

$$* U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

Discussion. The triclinic unit cell contains two sets of two crystallographic independent molecules (Fig. 1). As shown in Fig. 2 both molecules *A* and *B* are approximate mirror images. Relevant data on the geometry are given in Table 2. The observed conformation of both PNS rings approaches that of a skew-boat (Cremer & Pople, 1975) with torsion angles ranging from -2.9 (3) to 39.0 (3) $^\circ$ (molecule *A*) and -39.4 (3) to 2.2 (3) $^\circ$ (molecule *B*) and lowest asymmetry-parameter values $\Delta C_s = 5.9$ (2) $^\circ$ for P(11) and N(12) and $\Delta C_s = 8.4$ (2) $^\circ$ for P(21) and N(22) (Duax, Weeks & Rohrer, 1976). Puckering parameters are: $Q = 0.328$ (3) Å, $\theta = 117.4$ (5), $\varphi = 109.7$ (5) $^\circ$ (molecule *A*) and $Q = 0.331$ (3) Å, $\theta = 63.4$ (5), $\varphi = 285.5$ (5) $^\circ$ (molecule *B*). The phenyl rings display normal geometry: averages $[C(11)-C(16)] = 1.375$ (5),* $[C(17)-C(112)] = 1.376$ (4), $[C(21)-C(26)] = 1.374$ (6) and $[C(27)-C(212)] = 1.371$ (6) Å. In each molecule the two phenyl substituents are in *cis* positions with respect to the PNS ring and are approximately parallel with a mutual angle of 13.6 (2) $^\circ$ (molecule *A*) or 16.0 (1) $^\circ$ (molecule *B*). The S-O bonds are not coplanar with the phenyl rings as may be judged from the torsion angles $O(11)-S(11)-C(11)-C(12) = -37.7$ (3) (molecule *A*), $O(21)-S(21)-C(21)-C(22) = 39.9$ (4) (molecule *B*), $O(12)-S(12)-C(17)-C(112) = 75.0$ (3) (molecule *A*) and $O(22)-S(22)-C(27)-C(212) = -69.7$ (3) $^\circ$ (molecule *B*). The corresponding values found in *trans*-NPCl₂(NSOPh)₂ (van Bolhuis *et al.*, 1981) are $O(1)-S(1)-C(1)-C(2) = -4.4$ (6) $^\circ$ and $O(2)-S(2)-C(21)-C(22) = 31.5$ (6) $^\circ$. The torsion angles show that in the *cis* isomer one of the phenyl rings (in both molecules) is almost 'perpendicular' to the adjacent S-O bond, whereas in the *trans* isomer one of the SOPh moieties is almost coplanar. The angles between the bisector of the angle O-S-C and the related plane of the segment NSN are in a narrow range, 3.6 (2), 4.2 (2) $^\circ$ (molecule *A*) and 3.8 (2), 3.3 (2) $^\circ$ (molecule *B*). In the *trans* isomer these values were calculated as 5.6 (3) and 5.2 (3) $^\circ$ respectively. P and S atoms show a distorted tetrahedral geometry. The observed P-Cl bond lengths [average value 1.981 (2) Å] and Cl-P-Cl bond angles [average value 101.5 (1) $^\circ$] may be compared with those reported for related compounds (van de Grampel & Vos, 1969; Tucker & van de Grampel, 1974; Perales, Fayos, van de Grampel & de Ruiter, 1980; van Bolhuis *et al.*, 1981). Short C-H...O bonds (Berkovitch-Yellin & Leiserowitz, 1984) are $O(11)\cdots H(110)$ ($x, y-1, z$) = 2.41 (3) Å and $O(21)\cdots H(29)$ ($x, y-1, z$) = 2.59 (3) Å [sum of the van der Waals radii is 2.72 Å (Bondi, 1964)] and $O(11)\cdots Cl(21)$ ($1-x, 1-y, -z$) = 3.139 (2) Å (sum of the van der Waals radii is

* Throughout this paper the mean values and their standard errors have been calculated using the formulae given by Domenicano, Vaciago & Coulson (1979).

3.27 Å). From a more detailed comparison of bond lengths of P–N–S segments in *cis*-NPCl₂(NSOCl)₂ (van de Grampel & Vos, 1969) and *cis*-NPCl₂(NSOF)₂ (Tucker & van de Grampel, 1974) it can be concluded that the electronegativity of the SOF center is larger than that of the SOCl center. Apart from some minor differences which border on significance, the endocyclic N–P and N–S bond lengths in the title compound are equal, mean values 1.573 (3) and 1.575 (3) Å respectively. This means that the electron-attracting capacity of the SOPh group equals that of the PCl₂ group. Combining the data for compounds *cis*-NPCl₂(NSOX)₂, X = F, Cl, Ph, the following sequence in electron-attracting capacity can be set up



which is in line with the sequence of corresponding ³¹P chemical shifts. A not completely understood asymmetry of the ring skeleton of *trans*-NPCl₂(NSOPh)₂ (van Bolhuis *et al.*, 1981) and a lack of data for other *trans* isomers do not allow for a comparison between *cis*- and *trans*-NPCl₂(NSOX)₂ (X = F, Cl, Ph).

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Table 2. Data on the geometry of *cis*-NPCl₂(NSOPh)₂

Molecule A		Molecule B	
Bond distances (Å)			
S(11)–N(11)	1.559 (3)	S(21)–N(21)	1.566 (3)
S(11)–N(12)	1.580 (3)	S(21)–N(22)	1.583 (3)
S(12)–N(12)	1.579 (3)	S(22)–N(22)	1.582 (3)
S(12)–N(13)	1.577 (3)	S(22)–N(23)	1.574 (3)
P(11)–N(11)	1.582 (4)	P(21)–N(21)	1.576 (3)
P(11)–N(13)	1.568 (3)	P(21)–N(23)	1.571 (3)
P(11)–Cl(11)	1.986 (1)	P(21)–Cl(21)	1.982 (1)
P(11)–Cl(12)	1.976 (1)	P(21)–Cl(22)	1.979 (1)
S(11)–O(11)	1.431 (2)	S(21)–O(21)	1.429 (2)
S(12)–O(12)	1.427 (3)	S(22)–O(22)	1.426 (2)
S(11)–C(11)	1.761 (3)	S(21)–C(21)	1.754 (4)
S(12)–C(17)	1.764 (3)	S(22)–C(27)	1.761 (3)
C(11)–C(12)	1.379 (5)	C(21)–C(22)	1.375 (5)
C(12)–C(13)	1.392 (6)	C(22)–C(23)	1.386 (6)
C(13)–C(14)	1.353 (6)	C(23)–C(24)	1.343 (7)
C(14)–C(15)	1.376 (5)	C(24)–C(25)	1.353 (7)
C(15)–C(16)	1.380 (5)	C(25)–C(26)	1.380 (6)
C(11)–C(16)	1.376 (5)	C(21)–C(26)	1.375 (5)
C(17)–C(18)	1.371 (5)	C(27)–C(28)	1.381 (5)
C(18)–C(19)	1.386 (5)	C(28)–C(29)	1.370 (5)
C(19)–C(110)	1.362 (5)	C(29)–C(210)	1.358 (5)
C(110)–C(111)	1.370 (5)	C(210)–C(211)	1.377 (5)
C(111)–C(112)	1.373 (5)	C(211)–C(212)	1.381 (5)
C(17)–C(112)	1.390 (5)	C(27)–C(212)	1.373 (5)
Bond angles (°)			
Cl(11)–P(11)–Cl(12)	101.36 (6)	Cl(21)–P(21)–Cl(22)	101.63 (6)
Cl(11)–P(11)–N(11)	109.2 (1)	Cl(21)–P(21)–N(21)	110.1 (1)
Cl(11)–P(11)–N(13)	109.1 (1)	Cl(21)–P(21)–N(23)	108.7 (1)
Cl(12)–P(11)–N(11)	108.6 (1)	Cl(22)–P(21)–N(21)	108.6 (1)
Cl(12)–P(11)–N(13)	108.7 (1)	Cl(22)–P(21)–N(23)	108.4 (1)
N(11)–P(11)–N(13)	118.5 (2)	N(21)–P(21)–N(23)	118.2 (2)
N(11)–S(11)–N(12)	112.5 (2)	N(21)–S(21)–N(22)	112.6 (2)
N(11)–S(11)–C(11)	106.3 (2)	N(21)–S(21)–C(21)	105.9 (2)
N(12)–S(11)–C(11)	108.2 (2)	N(22)–S(21)–C(21)	107.4 (2)
O(11)–S(11)–N(11)	113.3 (2)	O(21)–S(21)–N(21)	113.2 (2)
O(11)–S(11)–N(12)	108.0 (2)	O(21)–S(21)–N(22)	108.0 (2)
O(11)–S(11)–C(11)	108.4 (1)	O(21)–S(21)–C(21)	109.4 (2)
N(12)–S(12)–N(13)	112.1 (2)	N(22)–S(22)–N(23)	112.0 (2)
N(12)–S(12)–C(17)	107.4 (2)	N(22)–S(22)–C(27)	108.0 (2)
N(13)–S(12)–C(17)	107.0 (2)	N(23)–S(22)–C(27)	107.0 (2)
O(12)–S(12)–N(12)	109.2 (2)	O(22)–S(22)–N(22)	108.9 (2)
O(12)–S(12)–N(13)	111.9 (2)	O(22)–S(22)–N(23)	112.2 (1)
O(12)–S(12)–C(17)	109.0 (2)	O(22)–S(22)–C(27)	108.5 (2)
S(11)–N(11)–P(11)	122.2 (2)	S(21)–N(21)–P(21)	122.5 (2)
S(11)–N(12)–S(12)	122.6 (2)	S(21)–N(22)–S(22)	122.5 (2)
S(12)–N(13)–P(11)	121.2 (2)	S(22)–N(23)–P(21)	121.5 (2)
S(11)–C(11)–C(12)	116.8 (3)	S(21)–C(21)–C(22)	116.9 (3)
S(11)–C(11)–C(16)	121.5 (3)	S(21)–C(21)–C(26)	122.0 (3)
C(12)–C(11)–C(16)	121.4 (3)	C(22)–C(21)–C(26)	120.9 (4)
C(11)–C(12)–C(13)	117.8 (3)	C(21)–C(22)–C(23)	118.5 (4)
C(12)–C(13)–C(14)	121.0 (3)	C(22)–C(23)–C(24)	120.1 (4)
C(13)–C(14)–C(15)	120.7 (4)	C(23)–C(24)–C(25)	121.8 (4)
C(14)–C(15)–C(16)	119.5 (4)	C(24)–C(25)–C(26)	119.6 (4)
C(11)–C(16)–C(15)	119.5 (3)	C(21)–C(26)–C(25)	119.0 (3)
S(12)–C(17)–C(18)	121.0 (3)	S(22)–C(27)–C(28)	121.1 (3)
S(12)–C(17)–C(112)	117.6 (3)	S(22)–C(27)–C(212)	117.8 (3)
C(18)–C(17)–C(112)	121.4 (3)	C(28)–C(27)–C(212)	121.1 (3)
C(17)–C(18)–C(19)	118.5 (3)	C(27)–C(28)–C(29)	119.2 (3)
C(18)–C(19)–C(110)	120.3 (4)	C(28)–C(29)–C(210)	120.8 (4)
C(19)–C(110)–C(111)	121.0 (4)	C(29)–C(210)–C(211)	119.8 (4)
C(110)–C(111)–C(112)	119.9 (3)	C(210)–C(211)–C(212)	120.8 (3)
C(17)–C(112)–C(111)	118.9 (3)	C(27)–C(212)–C(211)	118.3 (3)
Torsion angles (°)			
N(13)–P(11)–N(11)–S(11)	7.5 (3)	N(23)–P(21)–N(21)–S(21)	–8.7 (3)
N(11)–P(11)–N(13)–S(12)	–2.9 (3)	N(21)–P(21)–N(23)–S(22)	2.2 (3)
N(12)–S(11)–N(11)–P(11)	10.0 (3)	N(22)–S(21)–N(21)–P(21)	–8.0 (3)
N(11)–S(11)–N(12)–S(12)	–34.9 (3)	N(21)–S(21)–N(22)–S(22)	33.7 (3)
N(11)–S(11)–C(11)–C(16)	26.4 (3)	N(21)–S(21)–C(21)–C(26)	–22.9 (4)
O(11)–S(11)–C(11)–C(12)	–37.7 (3)	O(21)–S(21)–C(21)–C(22)	39.9 (4)
N(13)–S(12)–N(12)–S(11)	39.0 (3)	N(23)–S(22)–N(22)–S(21)	–39.4 (3)
N(12)–S(12)–N(13)–P(11)	–18.2 (3)	N(22)–S(22)–N(23)–P(21)	19.7 (3)
N(13)–S(12)–C(17)–C(18)	15.5 (4)	N(23)–S(22)–C(27)–C(28)	–11.8 (3)
O(12)–S(12)–C(17)–C(112)	75.0 (3)	O(22)–S(22)–C(27)–C(212)	–69.7 (3)

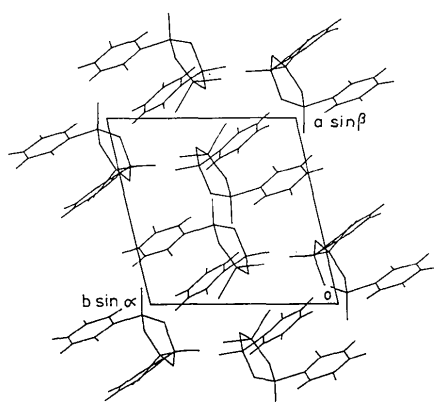


Fig. 1. Projection of the structure down [001].

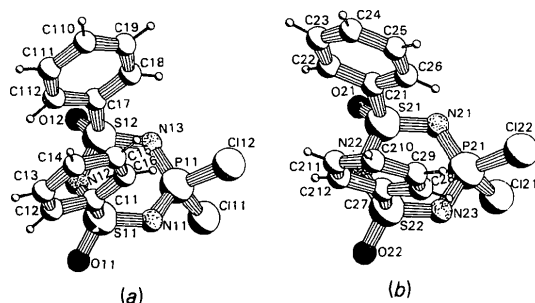


Fig. 2. PLUTO (EUCLID version) drawing of *cis*-NPCl₂(NSOPh)₂ illustrating the puckering and the adopted numbering scheme. (a) Molecule A. (b) Molecule B.

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Structure of *trans*-5-Isopropyl-1,3-diphenyl-5-propyl-1 λ^6 ,3 λ^6 ,2,4,6,5 λ^5 -dithiatriazaphosphorine 1,3-Dioxide

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Abstract. C₁₈H₂₄N₃O₂PS₂, $M_r = 409.5$, monoclinic, $P2_1/n$, $a = 13.432$ (6), $b = 16.727$ (4), $c = 9.602$ (2) Å, $\beta = 110.21$ (3)°, $V = 2025$ (1) Å³, $Z = 4$, $D_x = 1.343$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 3.5$ cm⁻¹, $F(000) = 864$, $T = 295$ K, $R = 0.053$ for 1628 observed reflections. The inorganic ring possesses a twist-boat conformation with the phenyl substituents in *trans* positions. Mean bond lengths are N–P = 1.608 (3), N–S (from segment SNS) = 1.568 (4), N–S (from segment PNS) = 1.544 (3) Å. The average endocyclic angles at S and N are 114.3 (2) and 124.4 (5)° respectively. The endocyclic angle at P amounts to 113.0 (2)°.

Introduction. To gather insights into the characteristics of cyclothiaphosphazenes we prepared a series of compounds, *trans*-NPRR'(NSOPh)₂. The N–S and N–P bonds within the ring skeleton are supposed to be strengthened by d_π – p_π interactions (van de Gramppe, 1981). The substituents R and R' most probably influence the contributions of 'π bonding' and hence the overall binding properties of these ring systems. Therefore it would be interesting to determine the bond lengths and angles of *trans*-NPRR'(NSOPh)₂ while varying R and R' along the electronegativity scale. The crystal and molecular structure of *trans*-NPRR'(NSOPh)₂ with two electron-withdrawing substituents ($R = R' = \text{Cl}$) is known (van Bolhuis, van den Berg & van de Gramppe, 1981), whereas the structure

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