

The Structure of 3,5,5-Trichloro-1-dimethylamino-1 λ^6 ,3 λ^6 ,2,4,6,5 λ^5 -dithiatriazaphosphorine 1,3-Dioxide, a Heterocycle Containing Sulphur, Phosphorus and Nitrogen Atoms

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Abstract

$C_2H_6Cl_3N_4O_2PS_2$ is orthorhombic, space group $P2_12_12_1$, with $a = 13.172$ (1), $b = 11.412$ (1), $c = 7.5070$ (3) Å, $Z = 4$. The structure was refined to $R = 0.031$ for 2443 independent reflexions. The endocyclic N–P and N–S lengths vary from 1.545 (2) to 1.603 (2) Å. The differences are explained in terms of the difference in the electronegativities of the P and S centres. The exocyclic N–S length is 1.599 (3) Å; the S–Cl length is 2.049 (1) Å. Average values for the P–Cl and S–O lengths are 1.967 (1) and 1.420 (2) Å, respectively.

Introduction

The chemistry of ring systems containing S, P and N atoms has become of increasing importance both from a theoretical (Faucher, van de Grampsel, Labarre, Nabi, de Ruiter & Shaw, 1977; van de Grampsel, 1977) and a chemotherapeutic (Sournies, 1979) point of view. The influence of the electronegativities of the substituents on the endocyclic bonding has been recognized in *cis*- $NPCl_2(NSOF)_2$ (Tucker & van de Grampsel, 1974), *cis*- $NPCl_2(NSOCl)_2$ (van de Grampsel & Vos, 1969) and $(NPCl_2)_2NSOCl$ (van Bolhuis & van de Grampsel, 1976). It has been suggested (van de Grampsel & Vos, 1969) that the d orbitals of S in the SOCl group are more involved in the $d_\pi-p_\pi$ bonding of the ring than are the d orbitals of P in the PCl_2 group due to the larger electronegativity of the former group. The replacement of Cl in the SOCl group by a less electronegative group, such as $N(CH_3)_2$, should decrease this effect. It will be shown that the endocyclic bond lengths of the title compound offer confirmation of this supposition.

Experimental

The preparation of the title compound ($NPCl_2NSOClNSONMe_2$) has been described by de Ruiter & van de

Grampsel (1978). The crystalline fraction obtained during this preparation appears to consist of two modifications, one with melting point 365–366 K, which was isolated fortuitously on one occasion, and another with melting point 406–407 K, the more easily isolable one. The two forms show somewhat different IR spectra (KBr pellets). No differences were observed in the 1H NMR spectra.

Suitable crystals of $NPCl_2NSOClNSONMe_2$ (m.p. 406–407 K) were obtained by careful cooling of an ether solution at 248 K. The crystal data are given in Table 1. The cell dimensions and the intensities of 2800 independent reflexions with $\theta < 25^\circ$ were measured on a four-circle diffractometer with a crystal $0.3 \times 0.3 \times 0.8$ mm, a $\theta/2\theta$ scan technique and graphite-monochromated Mo radiation. The intensities were corrected for Lorentz and polarization effects; absorption corrections were applied with a local version of *ORABS* (Wehe, Busing & Levy, 1962) (maximum and minimum correction factors were 1.84 and 1.34). 2457 reflections were classified as significant by the criterion $I > 2\sigma(I)$. 14 reflexions with unreliable intensities because of extinction were excluded. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Anomalous-dispersion corrections were applied for Cl, S and P.

Solution and refinement

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971) supplemented by the recycling procedure of Karle. The positions of the H atoms were determined from a difference synthesis. Refinement was carried out by full-matrix least squares with 2443 reflexions and anisotropic temperature parameters for all non-hydrogen atoms. After the first refinement the C(1) atom, *cis* to O(2) (Fig. 1), showed some abnormalities: positioned on the plane N(4)–

Table 1. *Crystal data*

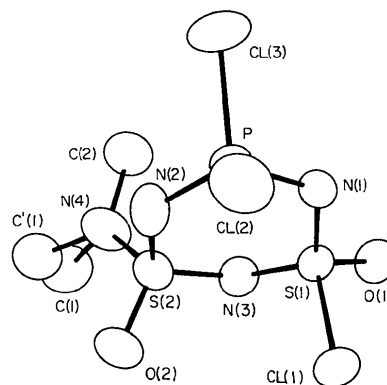
$C_2H_6Cl_3N_4O_2PS_2$	$M_r = 319.6$
Orthorhombic	Space group $P2_12_12_1$
$a = 13.172(1) \text{ \AA}$	$Z = 4$
$b = 11.412(1)$	$F(000) = 652$
$c = 7.5070(3)$	$\lambda(\text{Mo } K\alpha) = 0.7107 \text{ \AA}$
$V = 1128.4 \text{ \AA}^3$	$\mu(\text{Mo } K\alpha) = 1.247 \text{ mm}^{-1}$
$d_c = 1.87 \text{ Mg m}^{-3}$	

Table 2. *Fractional atomic coordinates (non-hydrogen atoms $\times 10^4$, H atoms $\times 10^3$)*

E.s.d.'s are given in parentheses. C(1), C'(1), H(3) and H(4) are half occupied.

	<i>x</i>	<i>y</i>	<i>z</i>
Cl(1)	2106 (1)	202 (1)	4743 (1)
Cl(2)	602 (1)	1953 (1)	8479 (1)
Cl(3)	-314 (1)	3961 (1)	6294 (2)
S(1)	1459 (0)	1573 (0)	3395 (1)
S(2)	-506 (0)	754 (1)	3573 (1)
P	240 (0)	2375 (1)	6013 (1)
O(1)	2194 (2)	1942 (2)	2134 (3)
O(2)	-604 (2)	-471 (2)	3878 (4)
N(1)	1246 (2)	2498 (2)	4850 (3)
N(2)	-583 (2)	1490 (3)	5307 (3)
N(3)	503 (2)	1070 (2)	2480 (3)
N(4)	-1394 (2)	1170 (3)	2268 (5)
C(1)	-1910 (10)	404 (14)	1176 (18)
C'(1)	-2236 (8)	456 (11)	1981 (19)
C(2)	-1464 (3)	2429 (4)	1888 (6)
H(1)	-207 (4)	-24 (4)	204 (7)
H(2)	-255 (4)	54 (4)	123 (6)
H(3)	-150 (6)	80 (8)	-1 (13)
H(4)	-284 (6)	68 (7)	301 (12)
H(21)	-199 (4)	255 (5)	140 (8)
H(22)	-88 (4)	262 (5)	173 (8)
H(23)	-163 (4)	273 (5)	292 (8)

C(2)—S(2), it vibrated strongly up and down from this plane [thermal parameters of C(1) in this direction were twice as large as those of C(2)]. Moreover, N(4)—C(1) = 1.36 Å was too short for a single bond. For these reasons, an alternative model was considered taking C(1) as 50% disordered between two possible positions for which N(4)—C(1) = 1.47 Å and the angles S(2)—N(4)—C(1) and C(2)—N(4)—C(1) are 117 and 113° respectively. This model was refined anisotropically by full-matrix least squares. The two half-occupied C atoms, C(1) and C'(1), converged at a mutual distance of 0.74 Å; they were the reflexion of each other with respect to the plane C(2)—N(4)—S(2), and showed thermal vibrations comparable to those of C(2). A difference synthesis revealed the H atoms of both C(1) and C'(1). Two of them, H(1) and H(2), lie on the plane C(2)—N(4)—S(2) and are shared by C(1) and C'(1), while H(3) and H(4), which are half-occupied, were found up and down from C(1) and C'(1), respectively. In the last refinement the following

Fig. 1. The molecular structure of NPCl₂NSOCINSONMe₂.

weighting scheme was used: $w = K/|f(F_o)|^2$, where $K = 0.5976$ and $f(F_o) = 0.6352 - 0.0922|F_o|$ when $|F_o| < 3.8$, $f(F_o) = 0.2923 + 0.0037|F_o|$ when $3.8 < |F_o| < 8.5$, and $f(F_o) = 0.1497 + 0.0176|F_o|$ when $8.5 < |F_o| < 99$. This weighting scheme produced $\langle w(F_o - F_c)^2 \rangle$ values independent of $\sin \theta$ and the magnitude of F_o (Martínez-Ripoll & Cano, 1975). In the last cycle R' was 0.030 ($R' = (\sum w\Delta^2 / \sum wF_o^2)^{1/2}$). The H atoms were assumed to vibrate isotropically and were given the B values of the C atoms to which they are bonded. R dropped to 0.031. Final atomic parameters are given in Table 2.* The molecular structure with the numbering of atoms is shown in Fig. 1.

Discussion

In the investigated isomer, which is the most abundant product of the reaction between *cis*-NPCl₂(NSOCl)₂ and Me₂NH (molar ratio 1:2) in acetonitrile, the O atoms are positioned *trans* with respect to each other. This confirms the structure assignment based on ¹H NMR shielding effects (de Rooter & van de Grampel, 1978). The O atom of the NSONMe₂ group no longer takes a position almost in the mean ring plane, as in *cis*-NPCl₂(NSOCl)₂, since the S centre is almost tetrahedral (Table 3). The SOCl group in both molecules remains almost unchanged. From the results obtained up to now it seems evident that substitution of a S-bonded Cl atom by an organic group leads to a drastic change in molecular geometry [*cf.* the structures of *trans*-NPCl₂(NSOPh)₂ (van den Berg *et al.*, 1979) and (NSOF)₂NSOPh (Arrington, Moeller & Paul, 1970)]. This geometry change in NPCl₂NSOCl-NSONMe₂ causes a completely different reaction

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34950 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Angles between the exocyclic bond from sulphur and the mean plane of the ring in NPCl₂-NSOCINSONMe₂ and *cis*-NPCl₂(NSOCl)₂

The equations of the planes in orthogonal space are $-0.3697 I + 0.7599 J - 0.5346 K = -0.4943$ and $-0.4663 I - 0.5695 J + 0.6769 K = -0.2206$. Average e.s.d. = 0.3° .

NPCl ₂ NSOCINSONMe ₂		<i>cis</i> -NPCl ₂ (NSOCl) ₂ *	
S(1)—O(1)	20.8°	S(1)—O(1)	35.5°
S(2)—O(2)	53.1	S(2)—O(2)	24.0
S(1)—Cl(1)	86.5	S(1)—Cl(3)	70.0
S(2)—N(4)	55.5	S(1)—Cl(4)	82.4

* Van de Grampel & Vos (1969).

Table 4. Some least-squares planes and distances (Å) of atoms to these planes

Atoms not included in the plane calculation are marked with an asterisk. E.s.d.'s are given in parentheses. The equations of the best planes are expressed in orthogonal space as $PI + QJ + RK = S$ (Nardelli, Musatti, Domiano & Andreotti, 1965).

$$\text{Plane I } -0.4519I + 0.7393J - 0.4991K = -0.3964$$

$$\text{Plane II } 0.9112I + 0.3937J - 0.1216K = 0.8172$$

Plane I		Plane II	
S(2)	-0.0053 (6)	Cl(2)	0.0085 (9)
P	0.0043 (6)	Cl(3)	0.010 (1)
N(1)	-0.056 (2)	P	-0.0119 (7)
N(2)	0.012 (3)	N(3)	0.041 (2)
N(3)	0.071 (2)	S(1)*	1.3310 (6)
S(1)*	-0.4170 (6)	S(2)*	-1.4115 (6)
		N(1)*	1.358 (2)
		N(2)*	-1.333 (2)

behaviour. While in its chloro precursor the formation of a five-coordinated P atom in an *S_N2*-type transition state is much hampered by steric interactions with the axial S-bonded Cl ligands [the reason why an *S_N1*-type mechanism at S can compete successfully with an *S_N2*-type one at P in acetonitrile (van den Berg, Klei, Kruk, de Ruiter & van de Grampel, 1976)], the geometry in NPCl₂NSOCINSONMe₂ offers sufficient space on both sides of the ring plane to permit an *S_N2*-type reaction. Indeed, reactions with dimethylamine (molar ratio 1:2) in diethyl ether as well as in acetonitrile lead to the formation of compounds with the formula NPCINMe₂NSOCINSONMe₂.

The conformation of the ring approaches that of an envelope (Table 4, distances to plane I). However, the shape of the ring is very asymmetric. This is not only apparent from the distances to the plane through P, Cl(1), Cl(2) and N(3) (Table 4, distances to plane II) but also from the differences in the endocyclic bond lengths. For example, in the segment S—N—S, bond lengths are observed which differ significantly from each other (Fig. 2). From a comparison with *cis*-NPCl₂(NSOX)₂ (X = F, Cl), where the corresponding

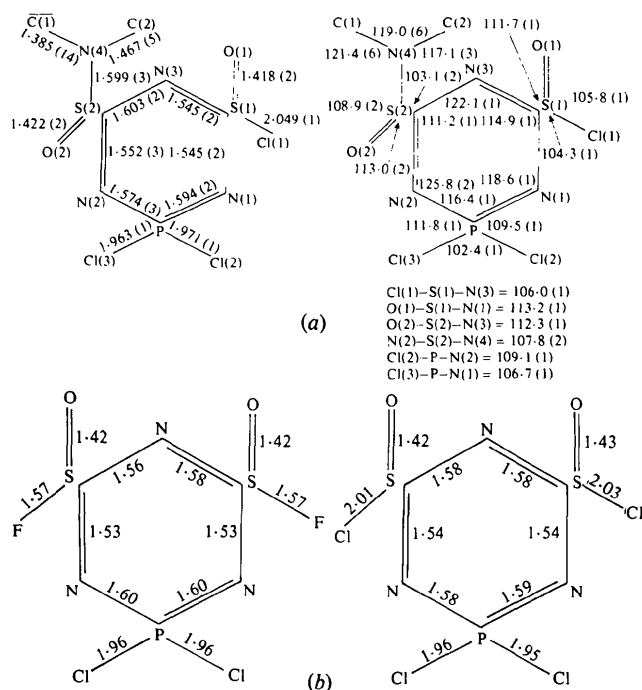


Fig. 2. (a) Bond lengths (Å) and angles (°) in NPCl₂NSOCl-NSONMe₂ (estimated standard deviations in parentheses; for numbering of atoms see Fig. 1). (b) Bond lengths (Å) in *cis*-NPCl₂(NSOF)₂ and *cis*-NPCl₂(NSOCl)₂.

S—N lengths are equal within experimental error, it is obvious that the introduction of the less electronegative (Huheey, 1965) NMe₂ group causes this perturbation of symmetry.

The endocyclic N—S and N—P bonds are shorter than the so-called single bonds in H₂NSO₃ (1.76 Å; Sass, 1960) and H₃NPO₃⁻ (1.77 Å; Cruickshank, 1964). This shortening can be explained both by changes in the hybridization of N, P and S and by the presence of *p*_π—*d*_π bonding between N and P and S (Craig & Paddock, 1971; Dewar, Lucken & Whitehead, 1960). It has been noticed for the ring systems *cis*-NPCl₂(NSOCl)₂ (van de Grampel & Vos, 1969) and (NPCl₂)₂NSOCl (van Bolhuis & van de Grampel, 1976) that an S(OCl) centre is more suitable for the formation of endocyclic π bonds than a P(Cl₂) centre. The difference (0.049 Å) between the N—P and N—S lengths in the segment P(Cl₂)—N—S(OCl) in NPCl₂NSOCINSONMe₂ agrees with these observations. The larger ability of the S(OCl) centre can be explained from the larger electronegativity of O compared with Cl (Craig & Magnusson, 1956). In the same way the N—S bonds in the segment S(OCl)—N—S(ONMe₂) differ significantly from each other. Here, the relatively small electronegativity of the NMe₂ group reduces the ability of the S centre concerned. Moreover, it can be understood that also the pronounced π bonding to N(4) exercises a negative in-

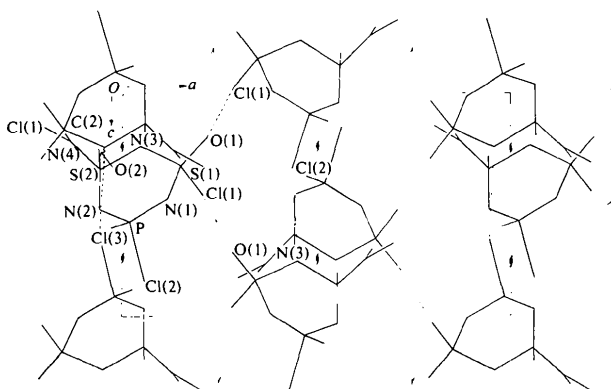


Fig. 3. Molecular packing of $\text{NPCl}_2\text{NSOCINSONMe}_2$ viewed down b . Dotted lines indicate intermolecular contacts: $\text{N}(3)\cdots\text{Cl}(2) = 3.173$ (2) and $\text{O}(1)\cdots\text{Cl}(1) = 3.174$ (2) Å.

fluence on the endocyclic bonding from $\text{S}(2)$. Although small, the difference (0.022 Å) between the lengths $\text{N}(2)\text{—}\text{S}(2)$ and $\text{N}(2)\text{—}\text{P}$ suggests that the $\text{S}(\text{ONMe}_2)$ centre is more active than the $\text{P}(\text{Cl}_2)$ centre. This leads to the following sequence in ability to form endocyclic bonds: $\text{S}(\text{OCl}) \gg \text{S}(\text{ONMe}_2) > \text{P}(\text{Cl}_2)$.

In Fig. 3 the projection of the structure along b is given. Two short non-bonding contacts are observed: $\text{Cl}(1)\cdots\text{O}(1)$ (3.17 Å; sum of the van der Waals radii 3.20 Å) and $\text{Cl}(2)\cdots\text{N}(3)$ (3.17 Å; sum of the van der Waals radii 3.30 Å). This means that each molecule interacts with four neighbours. From the proposed relationship between the number of intermolecular contacts and the melting point (van Bolhuis & van de Grampel, 1976), a relatively high melting point can be predicted for $\text{NPCl}_2\text{NSOCINSONMe}_2$. The experimental value 406–407 K fits in with this expectation.

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References

- ARRINGTON, D. E., MOELLER, TH. & PAUL, I. C. (1970). *J. Chem. Soc. A*, pp. 2627–2631.
- BERG, J. B. VAN DEN, VAN BOLHUIS, F., CNOSSEN-VOSWIJK, C., VAN DE GRAMPPEL, J. C., HETTINGA, A. M. G., HOEVE, W., DE RUITER, B. & WINTER, H. (1979). *Abstr. Int. Conf. Phosphorus Chem.*, Halle, Saale, DDR.
- BERG, J. B. VAN DEN, KLEI, E., KRUK, C., DE RUITER, B. & VAN DE GRAMPPEL, J. C. (1976). *Recl Trav. Chim. Pays-Bas*, **95**, 206–208.
- BOLHUIS, F. VAN & VAN DE GRAMPPEL, J. C. (1976). *Acta Cryst.* **B32**, 1192–1195.
- CRAIG, D. P. & MAGNUSSON, E. A. (1956). *J. Chem. Soc.* pp. 4895–4909.
- CRAIG, D. P. & PADDOCK, N. L. (1971). *Non-Benzenoid Aromatics*, Vol. II, pp. 273–357, edited by J. P. SNIJDER. New York, London: Academic Press.
- CRUICKSHANK, D. W. J. (1964). *Acta Cryst.* **17**, 671–672.
- DEWAR, M. J. S., LUCKEN, E. A. C. & WHITEHEAD, M. A. (1960). *J. Chem. Soc.* pp. 2423–2429.
- FAUCHER, J.-P., VAN DE GRAMPPEL, J. C., LABARRE, J.-F., NABI, S. N., DE RUITER, B. & SHAW, R. A. (1977). *J. Chem. Res. (S)*, p. 112; (*M*), pp. 1257–1294.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 365–376.
- GRAMPEL, J. C. VAN DE (1977). *Proc. Second Part First Int. Symp. Inorganic Ring Systems*, Madrid, pp. 364–385.
- GRAMPEL, J. C. VAN DE & VOS, A. (1969). *Acta Cryst.* **B25**, 651–656.
- HUHEEY, J. E. (1965). *J. Phys. Chem.* **69**, 3284–3291.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- MARTÍNEZ-RIPOLL, M. & CANO, F. H. (1975). *PESOS* program. Instituto 'Rocasolano', CSIC, Serrano 119, Madrid-6, Spain.
- NARDELLI, M., MUSATTI, A., DOMIANO, P. & ANDRETTI, G. (1965). *Ric. Sci.* **35**, 807–810.
- RUITER, B. DE & VAN DE GRAMPPEL, J. C. (1978). *Inorg. Chim. Acta*, **31**, 195–201.
- SASS, R. L. (1960). *Acta Cryst.* **13**, 320–324.
- SOURNIES, F. (1979). Thesis, Univ. Paul Sabatier, Toulouse, France.
- TUCKER, P. A. VAN DE GRAMPPEL, J. C. (1974). *Acta Cryst.* **B30**, 2795–2798.
- WEHE, D. J., BUSING, W. R. & LEVY, H. A. (1962). *ORABS*. Report ORNL-TM-229. Oak Ridge National Laboratory, Tennessee.