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Structure and Thermal Motion of Sulfonylbis(phosphorimidic trichloride), $\text{SO}_2(\text{NPCl}_3)_2$, at 100 K

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(Received 8 August 1994; accepted 4 October 1994)

Abstract

Sulfonylbis(phosphorimidic trichloride), $\text{SO}_2(\text{NPCl}_3)_2$, $M_r = 366.74$, monoclinic, $P2_1/c$, $a = 11.843(1)$, $b = 7.751(1)$, $c = 12.374(2)$ Å, $\beta = 95.11(1)^\circ$, $V = 1131.4(2)$ Å³, $Z = 4$, $D_x = 2.153$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71069$ Å, $\mu = 19.56$ cm⁻¹, $F(000) = 712$, $T = 100$ K, $R = 0.0284$, $wR = 0.0296$, $S = 1.33$ for 3806 unique observed reflections and 118 parameters. The P—N distances observed [1.5405(15) and 1.5342(14) Å] are the shortest of all compounds known to contain a non-cyclic S—N—P fragment. The S—N—P angles [129.56(10) and 132.27(9)°] are smaller than the bond angles observed in non-cyclic P—N—P compounds. The preference of the more folded conformation with approximate C_2 symmetry over the stretched conformation with $C_{2v}mm2$ symmetry is most probably due to some electron delocalization over the two almost planar O=S—N=P—Cl fragments. The N=P—Cl and O=S—N angles in these fragments [107.55(6), 108.12(6) and 105.54(7), 105.85(8)°, respectively] are markedly smaller than the remaining related angles [115.57(6)–117.56(6) and 110.57(8), 111.20(7)°, respectively]. Therefore, the angle between the O—S—O plane and the N—S—N plane [86.4(1)°] deviates significantly from 90°. The thermal motion of the molecule can best be described as almost independent

motions of rigid SO_2N_2 and NPCl_3 tetrahedra, coupled by a 'ball joint'.

1. Introduction

In the course of the structural investigations of the phosphorimidic trichlorides, $\text{Cl}_3\text{PNP}(\text{O})\text{Cl}_2$ (Belaj, 1993), $[\text{Cl}—\text{P}(\text{NPCl}_3)_3]^+\text{X}^-$ [$\text{X} = \text{Cl}^-, \text{PCl}_6^-$ (Belaj, 1992)] and $[\text{P}(\text{NPCl}_3)_4]^+\text{ICl}_2^-$ (Belaj, 1995), the structure determination of $\text{SO}_2(\text{NPCl}_3)_2$ was desired in order to study the flexibility of the NPCl_3 group at the N atoms. The title compound was synthesized for the first time by reaction of sulfamide with phosphopentachloride (Kirsanov, 1952); the hydrolysis (Haubold & Becke-Goehring, 1967), alcoholysis (Schöning, Klingebiel & Glemser, 1974) and several reactions with silylamines yielding open-chained and cyclic compounds (Becke-Goehring, Bayer & Mann, 1966; Klingebiel & Glemser, 1971, 1972) are described in the literature. No structural data are known for open-chained derivatives; the heterocyclic compound 1-methyl-bis(dichlorophosphazo)-sulphonamide, $\text{SO}_2(\text{NPCl}_2)_2\text{NCH}_3$, is the only derivative of $\text{SO}_2(\text{NPCl}_3)_2$ of which the crystal structure is known (Nuber & Ziegler, 1977). The non-rigid body motion of the exceptionally flexible cation in $[\text{P}(\text{NPCl}_3)_4]^+\text{ICl}_2^-$ could not be explained by intramolecular torsion. Despite

the difficulties arising from possible disorder, a model explaining the thermal motion in that cation has been presented (Belaj, 1995). This model is also applicable to the related title compound, in which disorder can be excluded.

2. Experimental

A colourless single crystal (0.30 × 0.40 × 0.45 mm) obtained by reaction of SO₂(NH₂)₂ with PCl₅ (Vandi & Moeller, 1966) was immersed in oil and immediately cooled to 100 K. All the data were gathered using graphite-monochromatized Mo K α radiation on a modified Stoe four-circle diffractometer with Nonius low-temperature equipment. The unit-cell constants were determined from a least-squares fitting to the circle angles of 40 well refined reflections (2θ range 25–27°). 5481 reflections were measured using ω -scans (scan range 1.2°) for 2θ from 3 to 70° (h -19→19, k 0→12, l 0→19), 3993 reflections with $I > 3\sigma(I)$, 3806 were unique. Two standard reflections (202, 114) were measured every 100 reflections. They showed maximum variations in intensity of 0.627% and 1.90%, respectively; the internal consistency factor was computed to $R_{\text{int}} = 0.0245$.

The data were corrected for L_p effects; the empirical absorption correction with *DIFABS* (Walker & Stuart, 1983) resulted in transmission factors of 0.881–1.240. The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1985), the full-matrix least-squares refinement on the F values with anisotropic displacement parameters for all atoms and a weighting scheme $w = 1/\sigma^2(F)$ until no parameter shifts occur gave $R = 0.0284$, $wR = 0.0296$ (3806 reflections, 118 parameters). The maximum and minimum peaks of the final difference-Fourier map were 0.502 and $-0.444 \text{ e } \text{\AA}^{-3}$, respectively.

Scattering factors and anomalous dispersion corrections from *International Tables for X-ray Crystallography* (Ibers & Hamilton, 1974). A DEC 7000-610 computer, and *ORTEP* (Johnson, 1965), *PLATON* (Spek, 1982), *SHELX76* (Sheldrick, 1976) and *THMI-2* (Schomaker & Trueblood, 1968; Dunitz & White, 1973; Trueblood, 1978) programs were used.

3. Discussion

The molecular structure and labelling scheme for SO₂(NPCl₃)₂ are shown in Fig. 1; a stereoview of the packing in the unit cell is provided in Fig. 2. Final atomic positional and displacement parameters are listed in Table 1,* and bond lengths and angles are given in

Table 2. The molecules lie on general positions and in rough approximation show C_{2v} symmetry (see Fig. 1), the twofold axis bisecting the O—S—O and N—S—N angles.

The P—N distances observed in the title compound are the shortest of all known compounds containing a non-cyclic S—N—P fragment and are comparable to the short P—N distances observed in compounds containing the N=P—Cl₃ group, as in the [Cl—P(N=P—Cl₃)₃]⁺ cation [1.502 (2), 1.534 (2) and 1.543 (2) Å; Belaj (1992)], the [Cl₃PNP—Cl₃]⁺ cation [1.513 (13)–1.561 (10) Å; Faggiani, Gillespie, Sawyer & Tyrer (1980)], Cl₃P=NP(O)Cl₂ [1.517 (3)–1.530 (3) Å; Belaj (1993)] or in the cyclic compound SO₂(NPCl₂)₂NCH₃ [1.542 (9) and 1.540 (8) Å; Nuber & Ziegler (1977)]. Due to the strong negative inductive effect of the three Cl atoms bonded to the P atoms, the mesomeric limiting formula expressing a $p\pi-d\pi$ bonding interaction of nitrogen p - and phosphorus d -orbitals (Cruickshank, 1961; Mitchell, 1969) is favoured over the ionic limiting formula, resulting in a distinct bond shortening. Due to the almost equal inductive withdrawing ability of Cl

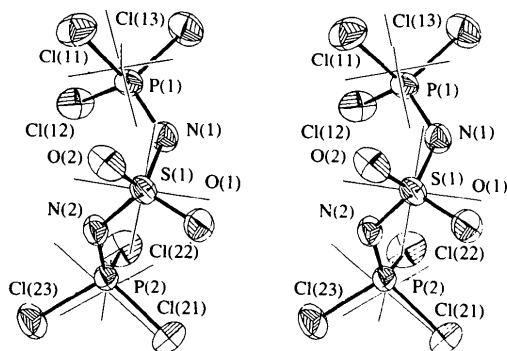


Fig. 1. Stereoscopic *ORTEP* (Johnson, 1965) plot of a SO₂(NPCl₃)₂ molecule showing the atomic numbering scheme. The probability ellipsoids are drawn at the 90% probability level. The directions of the eigenvectors of the librational tensors L for the SO₂N₂ group and the two NPCl₃ groups are drawn as thin lines, their lengths being proportional to the corresponding eigenvalues.

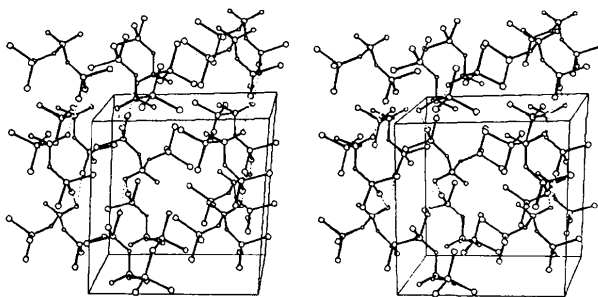


Fig. 2. Stereoscopic drawing of the packing of the molecules in the unit cell. The atoms are drawn as spheres with arbitrary radii. The two short intermolecular contacts Cl(13)···O(2) [2.901 (1) Å] and Cl(12)···O(2) [3.006 (1) Å] are drawn with dashed lines.

* A list of structure factors has been deposited with the IUCr (Reference: SE0160). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates ($\times 10^5$) and displacement parameters (in $\text{\AA}^2 \times 10^4$) with standard deviations in parentheses

The form of the temperature factor used is $T = \exp[-2\pi^2(h^2a^2U_{11} + \dots + 2hka^*b^*U_{12} + \dots)]$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	24576 (3)	45604 (5)	37388 (3)	172 (2)	110 (1)	116 (1)	-4 (1)	16 (1)	-6 (1)
O(1)	34458 (11)	52815 (16)	43184 (10)	257 (6)	172 (5)	183 (5)	-35 (5)	-56 (5)	-18 (4)
O(2)	14229 (11)	46128 (16)	42538 (10)	248 (6)	173 (5)	175 (5)	37 (5)	95 (4)	9 (4)
N(1)	23138 (12)	55512 (18)	25926 (11)	179 (6)	163 (6)	142 (5)	-29 (5)	8 (5)	27 (5)
P(1)	13286 (4)	54902 (5)	16924 (3)	152 (2)	147 (2)	131 (2)	10 (1)	14 (1)	15 (1)
Cl(11)	-2307 (4)	56230 (6)	21388 (4)	166 (2)	293 (2)	269 (2)	51 (2)	49 (1)	9 (2)
Cl(12)	12932 (4)	34414 (6)	7353 (3)	260 (2)	237 (2)	184 (2)	47 (2)	-20 (1)	-65 (2)
Cl(13)	14781 (4)	74748 (6)	7305 (4)	316 (2)	241 (2)	216 (2)	-16 (2)	-2 (2)	108 (2)
N(2)	26486 (11)	25610 (18)	34525 (12)	143 (5)	116 (5)	233 (6)	-9 (5)	39 (5)	-18 (5)
P(2)	36978 (3)	15535 (5)	31697 (3)	129 (2)	123 (2)	163 (2)	-1 (1)	16 (1)	1 (1)
Cl(21)	51495 (4)	20824 (6)	40230 (4)	160 (2)	287 (2)	272 (2)	-15 (2)	-44 (1)	0 (2)
Cl(22)	40604 (4)	16712 (7)	16433 (4)	252 (2)	410 (3)	180 (2)	27 (2)	66 (2)	-19 (2)
Cl(23)	34010 (4)	-9078 (5)	34028 (4)	242 (2)	115 (2)	445 (3)	4 (1)	43 (2)	14 (2)

Table 2. Bond distances (\AA), bond angles ($^\circ$) and selected torsion angles ($^\circ$) for $\text{SO}_2(\text{NPCl}_3)_2$

S(1)—O(1)	1.4307 (14)	Cl(11)—P(1)	1.9768 (7)
S(1)—O(2)	1.4312 (14)	Cl(12)—P(1)	1.9792 (7)
S(1)—N(1)	1.6085 (14)	Cl(13)—P(1)	1.9626 (7)
S(1)—N(2)	1.6102 (15)	Cl(21)—P(2)	1.9788 (7)
P(1)—N(1)	1.5405 (15)	Cl(22)—P(2)	1.9760 (7)
P(2)—N(2)	1.5342 (14)	Cl(23)—P(2)	1.9658 (6)
O(1)—S(1)—O(2)	117.41 (8)	Cl(13)—P(1)—N(1)	108.12 (6)
O(1)—S(1)—N(1)	105.85 (8)	Cl(11)—P(1)—Cl(12)	103.79 (3)
O(1)—S(1)—N(2)	111.20 (7)	Cl(11)—P(1)—Cl(13)	105.40 (3)
O(2)—S(1)—N(1)	110.57 (8)	Cl(12)—P(1)—Cl(13)	105.32 (3)
O(2)—S(1)—N(2)	105.54 (7)	Cl(21)—P(2)—N(2)	117.11 (6)
N(1)—S(1)—N(2)	105.75 (8)	Cl(22)—P(2)—N(2)	116.35 (6)
S(1)—N(1)—P(1)	129.56 (10)	Cl(23)—P(2)—N(2)	107.55 (6)
S(1)—N(2)—P(2)	132.27 (9)	Cl(21)—P(2)—Cl(22)	104.36 (3)
Cl(11)—P(1)—N(1)	117.56 (6)	Cl(21)—P(2)—Cl(23)	106.32 (3)
Cl(12)—P(1)—N(1)	115.57 (6)	Cl(22)—P(2)—Cl(23)	104.00 (3)
O(1)—S(1)—N(1)—P(1)	-171.55 (11)		
O(2)—S(1)—N(1)—P(1)	-43.41 (14)		
N(2)—S(1)—N(1)—P(1)	70.37 (13)		
O(1)—S(1)—N(2)—P(2)	-33.85 (15)		
O(2)—S(1)—N(2)—P(2)	-162.18 (12)		
N(1)—S(1)—N(2)—P(2)	80.60 (14)		
S(1)—N(1)—P(1)—Cl(11)	44.45 (13)		
S(1)—N(1)—P(1)—Cl(22)	-78.77 (12)		
S(1)—N(1)—P(1)—Cl(13)	163.53 (9)		
S(1)—N(2)—P(2)—Cl(21)	41.82 (15)		
S(1)—N(2)—P(2)—Cl(22)	-82.55 (13)		
S(1)—N(2)—P(2)—Cl(23)	161.35 (11)		

atoms relative to phenoxy substituents (Taft, Price, Fox, Lewis, Andersen & Davis, 1963), the P—N distance in $(\text{C}_6\text{H}_5\text{O})_3\text{P}=\text{NSO}_2\text{CH}_3$ (Blaschette, Jones, Naveke & Schulte-Korne, 1991), the S—N—P compound showing the hitherto shortest P—N distance, is only slightly larger [1.544 (3) \AA] than in $\text{SO}_2(\text{NPCl}_3)_2$. Taking the length of an 'ideal' P—N single bond of 1.800 (4) \AA observed in $\text{K}[\text{H}_3\text{N}-\text{PO}_3]$ (Cameron, Chan & Chute, 1980) as a basis, the bond order of the P—N bonds in $\text{SO}_2(\text{NPCl}_3)_2$ is calculated to be 1.75 and 1.78, respectively (Robinson, 1989).

The S—O and S—N bond lengths are slightly shortened and the O—S—O and N—S—N bond angles are diminished compared with the geometric

parameters [1.435 (1) and 1.627 (1) \AA , and 118.95 (7) and 111.37 (6) $^\circ$, respectively] determined in $\text{SO}_2(\text{NH}_2)_2$ (Belaj, Kratky, Nachbaur & Popitsch, 1987) at 100 K. The small but significant deviations from exact C_{2v} symmetry (see Table 2) are very probably due to short intermolecular Cl \cdots O interactions [Cl(23) \cdots O(1) 3.162 (1), Cl(21) \cdots O(1) 3.248 (1); Cl(13) \cdots O(2) 2.901 (1), Cl(12) \cdots O(2) 3.006 (1) \AA (see Fig. 2)], since the intramolecular interactions are almost equal in the two molecular moieties: There are two intramolecular contact distances [Cl(11) \cdots O(2) 3.223 (1) and Cl(21) \cdots O(1) 3.238 (1) \AA] shorter than 3.27 \AA , the sum of the van der Waals radii (Bondi, 1964).

A search in the Cambridge Structural Database (CSD, release date 03/03/94; Allen *et al.*, 1991) was carried out in order to study the flexibility of the S—N—P bond angle compared with P—N—P, ranging from 124.79 to 180 $^\circ$ (Belaj, 1995). Only 13 entries were found containing a non-cyclic S—N—P fragment. The S—N—P angles range from 118.63 to 136.29 $^\circ$ and show no correlation with the S—N distance, but a strong correlation (coefficient of correlation = -0.80) with the P—N distance (see Fig. 3).

In compounds containing the $X_2\text{O}_7$ molecule or ion ($X = \text{Cl}, \text{S}, \text{P}, \text{Si}$), the change in the X—O—X angle from 115 (in Cl_2O_7) to 180 $^\circ$ (Si_2O_7 group in thortveitite) can be correlated with the increasing role of the π -system in the inner bonds as the X—O—X angle approaches 180 $^\circ$ (Cruickshank, 1961). For species containing X—O—X bridges, the general increase in the bond angle was attributed to an increasing repulsion between the bonds along with increasing bond order (Gillespie & Robinson, 1964). The increasing bond order can be correlated with decreasing bond length and increasing stretching force constants, calculated from the vibrational frequencies (Robinson, 1963; Gillespie & Robinson, 1963). In the related compounds containing an X—N=X fragment ($X = \text{S}, \text{P}, \text{Si}$) with four-coordinated atoms X, a general increase in bond angle is to be expected in the order S—N=P < P—N=P < Si—N=P < Si—N=Si. In fact,

the mean values of the bond angles of these four types of compounds obtained from different searches in the CSD are 123.5 (10), 142.9 (4), 149 (5) and 168 (2)°, respectively. Although this trend in the data is obvious, the dependence on the type of substituent at X, the bias resulting from the overwhelming majority of bis(triphenylphosphine)iminium compounds containing a P—N=P group, and the small number of compounds containing the other fragments (13, 499, 7 and 4, respectively), must be considered.

The fact that the O(2)—S(1)—N(1) and O(1)—S(1)—N(2) angles are distinctly larger than the O(1)—S(1)—N(1) and O(2)—S(1)—N(2) angles, resulting in an angle between the O—S—O and N—S—N planes of 86.4(1)° [89.3(1)° in SO₂(NH₂)₂], and the fact that the Cl(11)—P(1)—N(1) and Cl(21)—P(2)—N(2) are somewhat larger than Cl(12)—P(1)—N(1) and Cl(22)—P(2)—N(2) angles could be interpreted as a repulsion between the Cl and O atoms for the intramolecular interactions Cl(11)···O(2) and Cl(21)···O(1), due to the negative atomic charges of both the Cl and the O atoms. However, the question then arises as to why this repulsion is not minimized by the rotation of the N=PCl₃ groups around the S—N single bonds, so the O(2)—S(1)—N(1)—P(1) and O(1)—S(1)—N(2)—P(2) torsion angles become *ca* 0°, with concomitant enlargement of the intramolecular

Cl···O distances. The differences in the O—S—N angles and the deviation of the angle between the O—S—O and N—S—N planes from 90° can be better attributed to electronic rather than steric effects (see below).

The eclipsed conformation with absolute Cl—P···S—O and Cl—P···S—N torsion angles not larger than 10.82(8)° is evidently determined by a gain in stability resulting from the almost planar *trans-trans* arrangement (*W* form) of the O(*n*)—S(1)—N(*n*)—P(*n*)—Cl(*n*3) fragments (*n* = 1, 2), although a *cis-trans* arrangement of the fragments would diminish possible intramolecular repulsive forces by appreciably larger contact distances. Such a *trans-trans* conformation (*W* form of Cl—P—N—P—X, X = O or Cl) is also observed in the two crystallographically independent cations of [Cl₃PNPCl₃][PCl₆] (Faggiani, Gillespie, Sawyer & Tyrer, 1980) and in the four independent molecules of Cl₃P=NP(O)Cl₂ (Belaj, 1993), and presumably is the result of some electron delocalization. In the [Cl—P(N=P(Cl)₃)₃]⁺ cation (Belaj, 1992), where this conformation is not possible by steric hindrance, *W* forms of the Cl—P—N—P—N fragments, besides a *cis-cis* conformation of a Cl—P—N—P—Cl fragment, were observed. In SO₂(NPCI₃)₂ the preference of the more folded conformation with approximate C₂ symmetry over the stretched conformation with C_{2v},*mm*2 symmetry (N—S—N—P torsion angles of 180°) is most probably due to the electron delocalization over the two O=S—N=P—Cl fragments.

The N—P—Cl bond angles of Cl(13) and Cl(23), the Cl atoms forming part of the *W* fragments, are markedly smaller than the others. In the crystal structure of [C(N=P(Cl)₃)₃]⁺SbCl₆⁻ (Müller, 1980), such bond angle differences are attributed to intramolecular repulsion between the N and Cl atoms of different N=P(Cl)₃ groups attached to the same C atom [three short N···Cl distances of 3.277–3.293 Å; *cf.* 3.30 Å, the sum of the van der Waals radii (Bondi, 1964)]. In SO₂(NPCI₃)₂, repulsion effects can be excluded between the N and Cl atoms [Cl(12)···N(2) 3.659(2) and Cl(22)···N(1) 3.890(2) Å], but possibly must be considered between the O and Cl atoms (see above). However, in Cl₃PNP(O)Cl₂ and the [Cl₃PNP(Cl)₃]⁺ cation, where an appreciable intramolecular repulsion can be excluded, the same bond angle discrepancy exists. A scatterplot of the N=P—Y bond angle α against the X—N=P—Y torsion angle τ in acyclic X—N=P—Y compounds (X = C, P or S; Y = C or Cl) found in the CSD shows a general decrease of α with increasing τ and two clusters at $\tau = 60$ and 180° [see Fig. 4(a)], as likewise discerned for carboxylic esters of tertiary alcohols (Schweizer, 1994). Analysis of the geometries of the larger number of bis(triphenylphosphine)iminium cations (130 precise structure determinations found in the CSD) resulted in the following: Besides the known

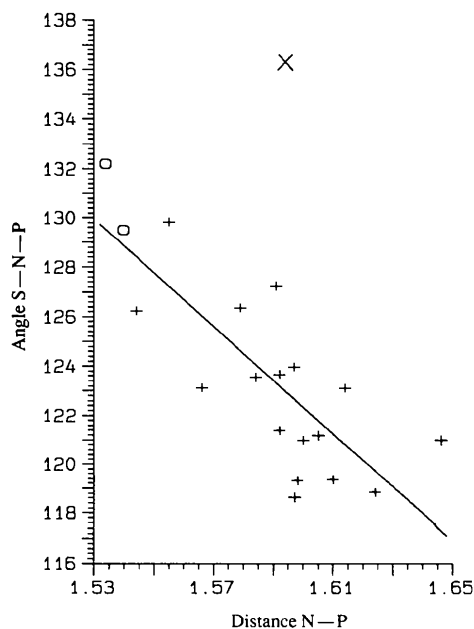


Fig. 3. Plot of the S—N—P angle (°) versus the N—P distance (Å) in acyclic S—N—P fragments found in the CSD (+, x) and in the title compound (o). The regression line is computed neglecting the outlier X produced by an intramolecular stacking interaction between a polyfluorinated phenyl group and another phenyl group attached to the P atom (Zibarev, Gatilov, Bagryanskaya, Maksimov & Miller, 1993).

correlation (Wilson & Bau, 1974; Belaj, 1995) between the P=N distance and the P=N=P angle [coefficient of correlation (C. of C.) = -0.763], there is a strong negative correlation between the N=P-C angle and the P=N=P-C torsion angle τ [see Fig. 4(b), C. of C. = -0.951], but no correlation between the N=P-C and P=N=P angles (C. of C. = 0.005) or between the N=P-C angle and the P=N distance (C. of C. = 0.004). Due to the periodicity of the rotation around the N=P bond, the dependence of the N=P-C angle as a function of τ is cosinusoidal rather than linear.

The non-equivalence of the Cl atoms is reflected to a smaller degree in the P-Cl bond lengths: In $\text{SO}_2(\text{NPCl}_3)_2$ they are significantly smaller at the Cl

atoms in the *W* fragments. This does not always hold true for the related compounds mentioned above, but is the case if the equivalent P-Cl bond lengths are averaged (difference 0.007–0.012 Å).

The deviation of the angle between the O-S-O and N-S-N planes from 90° in $\text{SO}_2(\text{NPCl}_3)_2$ can now be explained by electronic effects: Due to some electron delocalization over the two O=S-N=P-Cl fragments, not only the N=P-Cl but also the O=S-N angles in these fragments are smaller than the remaining related angles. This conclusion is supported by the structure of $\text{Cl}_3\text{PNP}(\text{O})\text{Cl}_2$ having four molecules in the asymmetric unit: In the three molecules showing the O=P-N=P-Cl fragment in the *W* form, the O=P-N angles range from 115.7(2) to 115.8(2)°; in the fourth molecule showing a Cl-P-N=P-Cl fragment in the *W* form, the O=P-N angle is 120.5(2)°.

The thermal motion analysis exhibits good quality displacement parameters (see Table 1), since they fulfil the 'rigid-bond' test (Hirshfeld, 1976; Dunitz, Maverick & Trueblood, 1988): The differences $\Delta = |z_{A,B}^2 - z_{B,A}^2|$ for every covalently bonded pair of atoms *A* and *B*, where $z_{A,B}^2$ denotes the mean-square amplitude of vibration of the atom *A* along the direction of the bond *A-B*, are not larger than 0.0005(6) Å², except for P(1)-N(1) [0.0011(6) Å²]. The rigid-body motion analysis (Schomaker & Trueblood, 1968) indicates that the molecule as a whole is not a rigid body: the residual index R_u , defined as $R_u = [\sum w(\Delta U)^2 / \sum w(U_{\text{obs}})^2]^{1/2}$, with $w = 1/\sigma^2$, is 0.144; the maximum difference Δ between non-bonded pairs of atoms is 0.0148(3) Å². On the other hand, the SO_2N_2 tetrahedron and the two NPCl_3 tetrahedra behave very well as rigid bodies [$R_u = 0.011, 0.014, 0.016$; $\Delta_{\text{max}} = 0.0007(8), 0.0013(3)$ and 0.0013(3) Å², respectively]. The applied absorption correction produces significant changes, mainly for the displacement parameters U_{22}, U_{33} and U_{13} [maximum value of $\Delta/(\sigma_1^2 + \sigma_2^2)^{1/2} = 12.6$] of the third-row elements, but only has small effects on the rigid-body motion analysis. Proceeding from uncorrected data, the related R_u values are 0.154 and 0.015, 0.015, 0.016, respectively.

Fig. 1 shows the directions of the eigenvectors of the librational tensors *L* for the three tetrahedra and the magnitude of their eigenvalues. The orientations of the eigenvectors indicate that the non-rigid body motion of the molecule cannot be described by intramolecular torsion about bonds (e.g. about the S-N single bonds). The librational eigenvectors having the smallest eigenvalues are oriented approximately parallel to the twofold molecular axis (for the SO_2N_2 group) or normal to the S-N-P planes (for the NPCl_3 groups), since librations around these vectors are strongly hindered by stretching/compressing the N-P or N-S bonds, respectively. The thermal motion of the molecule resulting from the high flexibility at the N atoms can best be described as

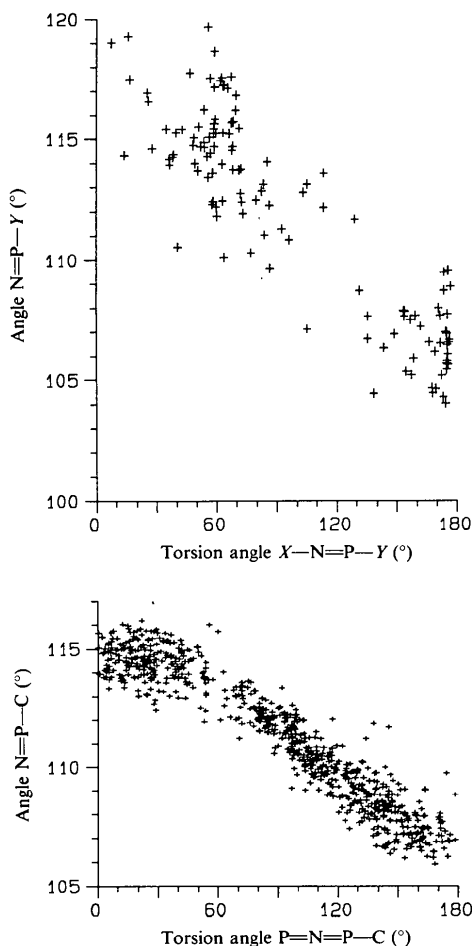


Fig. 4. (a) Plot of the N=P-Y bond angle α (°) versus the absolute value of the X-N=P-Y torsion angle τ in acyclic X-N=P-Y compounds (*X* = C, P or S; *Y* = C or Cl) found in the CSD (37 precise structure determinations with $R \leq 0.08$ and the average sigma of a C-C bond ≤ 0.01 Å). (b) Plot of the N=P-C bond angle α (°) versus the absolute value of the P=N=P-C torsion angle τ in bis(triphenylphosphine)iminium cations (130 precise structure determinations found in the CSD with $R \leq 0.08$ and the average sigma of a C-C bond ≤ 0.01 Å).

almost independent motions of rigid tetrahedra, coupled by a 'ball joint', as stated for Cl₃PNP(O)Cl₂ and for the [Cl—P(NPCl₃)₃]⁺ and [P(NPCl₃)₄]⁺ cations (Belaj, 1995).

The author thanks Associate Professor Dr Ch. Kratky, Institute of Physical Chemistry, University of Graz, for the use of the diffractometer.

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