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The Crystal Structure of $NPCl_2(NSOCl)_2$

By J. C. van de Grampel and Aafje Vos

Laboratorium voor Structuurchemie, Rijksuniversiteit Groningen, Bloemsingel 10, *Groningen, The Netherlands*

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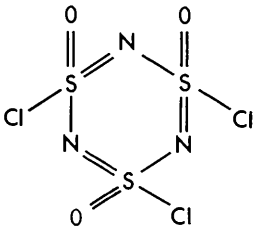
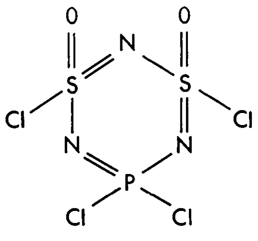
Crystals of cyclo-tri-μ-nitrido-dichlorophosphorus-bis(oxochlorosulphur), $NPCl_2(NSOCl)_2$, are monoclinic, space group $P2_1/n$. The cell dimensions are $a=11·649$, $b=7·705$, $c=11·092$ Å, $\beta=101·37$, $Z=4$ units $NPCl_2(NSOCl)_2$. The structure was determined from a three-dimensional Patterson synthesis and refined by anisotropic least-squares analysis of 1010 independent reflexions, $R=0·044$. The molecules contain a six-membered ring of P, N and S atoms in the sequence -N-P-N-S-N-S-. The phosphorus atom carries two chlorine atoms and each sulphur atom is linked to one oxygen and one chlorine atom. Mean bond lengths, with estimated standard deviations for the individual values in parentheses, are N-P = 1·585 (0·013), P-Cl = 1·957 (0·006), S-Cl = 2·018 (0·006) and S-O = 1·421 (0·013) Å. The N-S bond lengths differ slightly and can be divided into two groups. Average values are 1·578 (0·013) Å for the N-S bonds of the group S-N-S and 1·540 (0·013) Å for the remaining N-S bonds. The endocyclic angles at P and S are 115·3 (0·7)° and 115·0 (0·7)° respectively. The angle S-N-S is 120·3 (0·8)°; for the angles P-N-S values of 123·5 (0·8)° and 120·6 (0·8)° were obtained.

Introduction

In addition to the structure of α-sulphanuric chloride (see I; Hazell, Wiegers & Vos, 1966), it was thought interesting to investigate the structure of β-sulphanuric chloride. Attempts to prepare the latter compound by thermal decomposition of Cl_3PNSO_2Cl according to Kirsanov (1952) failed, however.



I



II

Instead, a compound of composition $PN_3S_2Cl_4O_2$ was obtained by applying Kirsanov's method in a slightly modified way (van de Grampel & Vos, 1963). We tentatively assumed the compound to be $NPCl_2(NSOCl)_2$ (II), *i.e.* $(NSOCl)_3$ with one of the SOCl groups replaced by PCl_2. This hypothesis was confirmed by the X-ray work described in this paper.

Experimental

$NPCl_2(NSOCl)_2$ (van de Grampel & Vos, 1963) was recrystallized from light petroleum. The colourless needles obtained (m.p. 94.9–95·9 °C) appeared to be stable to moist air and to irradiation by X-rays.

The unit cell is monoclinic, space group $P2_1/n$ with $a=11·649 \pm 0·003$, $b=7·705 \pm 0·003$, $c=11·092 \pm 0.003$ Å, $\beta=101.37 \pm 0·13$°, $Z=4$ formula units, $D_x=2·13$ g.cm^{-3}, $D_m=2·14$ g.cm^{-3}, $\mu(\text{Mo})=17.8$ cm^{-1}. The needle axis of the crystals coincides with the **b** direction. The cell dimensions were obtained from a powder diffractogram recorded with the Philips diffractometer PW1050/30, silicon lines being used for calibration [$\lambda(\text{Cu } K\alpha)=1·5418$ Å].

For the intensity measurements a single crystal of dimensions 0·22 × 0·23 × 0·39 mm was mounted in a Hanff capillary. Integrated equi-inclination Weissenberg photographs about the b axis were taken for $k=0$ to 8 with zirconium filtered molybdenum radiaton. Use was made of the multiple film technique. The reflexions $0k0$ were obtained from the zero layer about [101]. For 1146 independent reflexions non-zero intensities were measured with a densitometer (Smits & Wiebenga, 1953). No corrections for absorption were applied ($\mu R \simeq 0·2$).

To put the $|F|^2$ values on the same scale each k layer was compared with the first layer about the b axis by recording parts of the integrated equi-inclination Weissenberg photographs of the two layers on the same photographic film. Care was taken that all the experimental conditions, such as the output of the X-ray tube, the integrated area and the exposure time, were kept the same for the two layers. To correct for the difference in path length through the film due to the difference in equi-inclination angle (ν_k and ν_1 for layer k and layer 1 respectively) the intensities of the kth layer were multiplied by $(\cos \nu_1)/(\cos \nu_k)$. After correction for this factor comparison of the different photographs obtained gave the scaling factor for all k layers.

Determination of the structure

The four molecules lie at general positions in the unit cell. Approximate coordinates for the P,N,S and Cl atoms could be found from a three-dimensional Patterson synthesis calculated with the 1146 independent reflexions with non-zero intensity. The x and z parameters of the oxygen atoms were determined from an [010] error synthesis and the y parameters of these atoms were estimated from the assumed geometry of the molecule. Preliminary two-dimensional refinement in the [010] projection was carried out by successive cycles of difference Fourier syntheses and structure factor calculations.

During the three-dimensional least-squares refinement 136 reflexions with unreliable intensities, because of extinction or strong variation in background, were not considered. These reflexions are marked with an asterisk in Table 3. The isotropic least-squares refinement was carried out on a Zebra computer using Schoone's program (Schoone, 1961), $R=0·094$. At this stage of the refinement a three-dimensional difference Fourier synthesis clearly showed the thermal motion of the atoms to be anisotropic.

Most cycles of the anisotropic least-squares refinement were done by Rollett on the Mercury computer in Oxford (Rollett, 1961). The last few cycles were calculated on a TR4 computer with a program written by Palm & Peterse according to Cruickshank's scheme (Cruickshank, 1961*a*). For this part of the refinement the atomic scattering factors used were those from Moore (1963). The weighting scheme adopted was

$$w=[1+\{(|F(\text{obs})|-23)/23\}^2]^{-1}\ .$$

After the refinement the value of $w|\Delta F|^2$ appeared to be independent of $|F(\text{obs})|$. The index R dropped to 0·044.

Table 1. *Fractional atomic coordinates with standard deations (in parentheses) in units of the last decimal position as calculated by the least-squares program*

	x	y	z
P	−0·1701 (2)	0·1539 (3)	−0·0514 (2)
N(1)	−0·0566 (5)	0·2073 (9)	0·0454 (5)
N(2)	−0·1608 (5)	0·4879 (8)	0·1074 (5)
N(3)	−0·2745 (5)	0·2894 (9)	−0·0683 (5)
S(1)	−0·0528 (2)	0·3606 (3)	0·1349 (2)
S(2)	−0·2830 (2)	0·4224 (2)	0·0335 (2)
Cl(1)	−0·2230 (2)	−0·0752 (3)	−0·0081 (2)
Cl(2)	−0·1296 (2)	0·1201 (3)	−0·2125 (2)
Cl(3)	−0·0621 (2)	0·2524 (3)	0·2973 (2)
Cl(4)	−0·3583 (2)	0·2951 (3)	0·1579 (2)
O(1)	0·0531 (5)	0·4559 (9)	0·1554 (6)
O(2)	−0·3576 (5)	0·5657 (8)	−0·0090 (5)

In Tables 1 and 2 the final parameters with standard deviations as calculated by the least-squares program are listed. The calculated structure factors in Table 3 are based on the parameters of Tables 1 and 2. As the molecule could not be considered as a rigid body (see discussion) the coordinates were not corrected for libration effects.

Discussion of the structure

Molecular structure

The molecule $NPCl_2(NSOCl)_2$ is shown in Fig. 1. The bond lengths and angles and their estimated standard deviations are listed in Table 4. In calculating these standard deviations with the formulae of Cruickshank & Robertson (1953), the standard deviations in the coordinates obtained from the least-squares program (Table 1) were multiplied by a factor of two.

The six-membered ring of the molecule is not completely planar, but has a deformed chair shape (Fig. 2). As may be seen from Table 5, N(1) lies in the plane through P, S(1) and S(2), whereas N(2) and N(3) are at

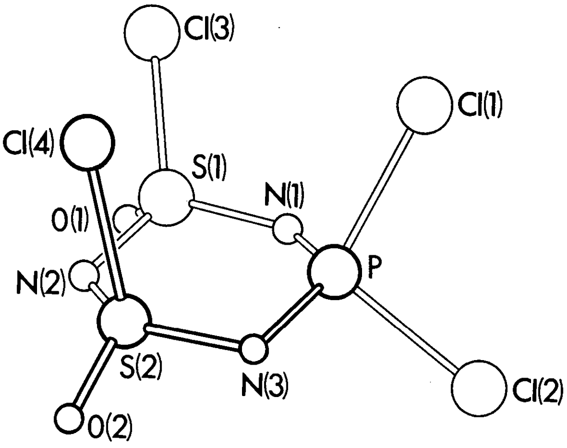


Fig. 1. Molecule of $NPCl_2(NSOCl)_2$.

Table 2. *Thermal parameters U_{ij} (in 10^{-4}Å^2) of the anisotropic temperature factor*

Standard deviations are given in parentheses.

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{31}$
P	362 (9)	352 (19)	314 (8)	26 (16)	−37 (16)	171 (13)
N(1)	379 (32)	453 (39)	405 (32)	128 (55)	−63 (53)	128 (51)
N(2)	452 (34)	295 (34)	378 (30)	125 (54)	−95 (51)	65 (51)
N(3)	338 (30)	500 (40)	333 (29)	−43 (55)	−138 (52)	2 (46)
S(1)	336 (8)	424 (10)	307 (7)	−160 (16)	51 (15)	76 (12)
S(2)	396 (9)	355 (10)	296 (7)	197 (16)	69 (14)	198 (13)
Cl(1)	812 (16)	359 (12)	845 (17)	−190 (22)	8 (22)	573 (27)
Cl(2)	753 (14)	630 (15)	354 (9)	206 (23)	−193 (18)	351 (18)
Cl(3)	512 (11)	796 (16)	335 (8)	186 (22)	347 (20)	79 (15)
Cl(4)	504 (11)	714 (15)	607 (12)	153 (22)	406 (22)	567 (20)
O(1)	448 (32)	787 (49)	661 (38)	−390 (61)	88 (69)	−40 (55)
O(2)	576 (33)	527 (35)	426 (28)	389 (55)	222 (53)	177 (50)

Table 3. *Comparion of* 10F(obs) *and* 10F(calc)

Reflexions marked by an asterisk were not included in the refinement.

H	K	L	FO	FC
-14	0	0	157	169
-12	0	0	249	-198 *
-10	0	0	544	-569
-8	0	0	350	-341
-4	0	0	359	-352
-2	0	0	700	-642 *
-11	0	1	341	328
-9	0	1	479	-487
-7	0	1	378	-392
-5	0	1	359	-356
-3	0	1	387	-371
-1	0	1	405	367 *
1	0	1	958	841 *
3	0	1	792	758
5	0	1	525	537
7	0	1	212	198
9	0	1	461	-485
13	0	1	230	-249
-10	0	2	258	232
-6	0	2	258	-245
-4	0	2	470	457
-2	0	2	866	-836 *
0	0	2	838	774 *
2	0	2	2396	-2229 *
4	0	2	1069	1066
6	0	2	405	394
-13	0	3	295	301
-9	0	3	295	-303
-7	0	3	249	249
-5	0	3	147	144
-3	0	3	525	-557
-1	0	3	295	-279
11	0	3	249	257
-14	0	4	166	177
-12	0	4	203	206
-10	0	4	157	161
-6	0	4	212	202
-4	0	4	498	-516
-2	0	4	1640	-1640
0	0	4	461	471
4	0	4	746	743
6	0	4	286	-285
8	0	4	240	245
10	0	4	240	249
-11	0	5	193	-197
-9	0	5	682	710
-7	0	5	332	347
-5	0	5	627	-613
-3	0	5	138	151
-1	0	5	184	187
1	0	5	986	-990
3	0	5	378	-401
5	0	5	461	464
-12	0	6	313	-324
-10	0	6	258	-229
-6	0	6	322	290
-4	0	6	111	-111
-2	0	6	912	913
0	0	6	682	667
2	0	6	765	-788
6	0	6	424	-434
-13	0	7	193	190
-11	0	7	184	-193
-7	0	7	663	-667
-3	0	7	783	805
1	0	7	147	143
3	0	7	571	556
5	0	7	267	290
7	0	7	221	-659 *
9	0	7	166	-152
-14	0	8	184	163
-12	0	8	212	-178
-4	0	8	488	-501
4	0	8	553	583
6	0	8	147	-125
-13	0	9	230	222
-11	0	9	378	-373
-9	0	9	230	210
-7	0	9	138	135
-3	0	9	203	-182
-1	0	9	221	-223
1	0	9	240	227
3	0	9	221	-212
9	0	9	221	217
-10	0	10	286	271
-8	0	10	184	-180
-6	0	10	157	-133
-4	0	10	286	-298
0	0	10	120	-113
8	0	10	230	234
-9	0	11	534	556
-7	0	11	304	-294
-5	0	11	221	-237
-1	0	11	387	-384
1	0	11	193	-174
5	0	11	304	298
-6	0	12	359	364
-4	0	12	203	186
-2	0	12	166	-136
0	0	12	396	-418
8	0	12	221	207
-7	0	13	184	-182
-5	0	13	387	392
-3	0	13	230	233
1	0	13	157	137
5	0	13	184	-191
2	0	14	175	168
-10	1	0	396	410
-9	1	0	424	432
-8	1	0	396	-396
-6	1	0	221	-214
-5	1	0	405	401
-4	1	0	1050	-1019
-3	1	0	1649	-1401 *
-2	1	0	903	-857
-1	1	0	295	238 *
-14	1	1	138	-132
-12	1	1	120	133
-11	1	1	111	112
-9	1	1	184	192
-8	1	1	203	163 *
-7	1	1	470	467
-6	1	1	111	-116
-5	1	1	83	94
-3	1	1	1456	-1277
-2	1	1	240	241
-1	1	1	1677	-1225 *
0	1	1	488	-498
1	1	1	608	552
2	1	1	746	-683
3	1	1	921	-881
4	1	1	184	193
5	1	1	92	-108
6	1	1	166	170
7	1	1	894	911
9	1	1	313	321
12	1	1	157	156
-11	1	2	184	-186
-10	1	2	387	398
-9	1	2	193	176 *
-8	1	2	442	-443
-7	1	2	350	-359
-6	1	2	341	332
-5	1	2	369	388
-4	1	2	332	322
-3	1	2	350	-325
-2	1	2	166	-104 *
-1	1	2	1271	1081 *
0	1	2	341	-339
1	1	2	507	-461
2	1	2	479	-460
3	1	2	387	-391
4	1	2	147	-149
5	1	2	765	757
6	1	2	304	-295
7	1	2	507	-521
8	1	2	332	334
12	1	2	230	237
-11	1	3	212	194
-10	1	3	405	-425
-9	1	3	221	224
-7	1	3	166	-157
-5	1	3	387	-380
-4	1	3	212	214
-2	1	3	276	287
-1	1	3	249	240
0	1	3	470	461
1	1	3	295	-296
2	1	3	147	144
3	1	3	295	-293
4	1	3	276	265
5	1	3	516	511
6	1	3	101	-107
7	1	3	120	153 *
8	1	3	415	-435
9	1	3	350	-380
-12	1	4	157	157
-11	1	4	240	-254
-9	1	4	157	-161
-8	1	4	138	-132
-7	1	4	46	-95 *
-6	1	4	995	1005
-5	1	4	488	485
-3	1	4	931	-921
-2	1	4	1014	-962
-1	1	4	1115	1062
0	1	4	147	-125 *
1	1	4	525	519
4	1	4	166	-157
5	1	4	46	52 *
7	1	4	350	-359
8	1	4	212	220
11	1	4	184	-166
-10	1	5	157	-167
-9	1	5	276	-285
-8	1	5	249	276 *
-6	1	5	405	-400
-5	1	5	746	756
-4	1	5	221	-187 *
-3	1	5	138	122
-2	1	5	92	114 *
-1	1	5	267	278
0	1	5	424	406
2	1	5	212	-218
3	1	5	212	-207
4	1	5	101	103
5	1	5	276	-278
6	1	5	221	231
7	1	5	249	-248
8	1	5	157	-161
11	1	5	166	156
-10	1	6	212	-219
-9	1	6	175	181
-6	1	6	212	-104 *
-4	1	6	691	-691
-3	1	6	691	-678
-2	1	6	553	556
-1	1	6	424	420
0	1	6	857	834
1	1	6	433	-444
5	1	6	221	222
6	1	6	138	144
7	1	6	147	133
8	1	6	221	-231
9	1	6	157	143
10	1	6	203	-207
-13	1	7	193	193
-12	1	7	175	168
-8	1	7	120	153 *
-6	1	7	359	-359
-5	1	7	212	-125 *
-4	1	7	405	404
-3	1	7	820	-813
-2	1	7	378	-358
-1	1	7	240	229
0	1	7	516	-492
1	1	7	166	-96 *
2	1	7	101	-106
4	1	7	240	244
5	1	7	424	436
7	1	7	193	211
10	1	7	203	197
-12	1	8	240	218
-9	1	8	120	110
-6	1	8	166	148
-5	1	8	249	236
-4	1	8	55	81 *
-3	1	8	276	-286
-2	1	8	46	92 *
0	1	8	654	-682
1	1	8	332	-342
2	1	8	249	-250
3	1	8	295	300
4	1	8	74	105 *
5	1	8	157	-164
6	1	8	138	166 *
9	1	8	175	164
10	1	8	203	191
-11	1	9	147	-141
-8	1	9	313	312
-7	1	9	101	115
-6	1	9	120	-153
-4	1	9	249	250
-3	1	9	193	-197
-2	1	9	147	-143
-1	1	9	332	339
1	1	9	249	-252
4	1	9	55	-76
6	1	9	138	-102
7	1	9	147	-152
-13	1	10	92	-142 *
-12	1	10	138	156
-10	1	10	157	-156
-8	1	10	193	191
-6	1	10	258	259
-4	1	10	341	-342
-3	1	10	55	82
-2	1	10	83	-104
-1	1	10	322	325
1	1	10	175	-161
2	1	10	120	147
3	1	10	101	118
5	1	10	240	-238
-9	1	11	258	237
-7	1	11	138	119
-6	1	11	369	-383
-4	1	11	295	308
-3	1	11	64	88
-2	1	11	101	142
-1	1	11	74	135 *
1	1	11	378	-385
3	1	11	147	-154
-10	1	12	175	-142
-8	1	12	64	116 *
-4	1	12	64	103
-2	1	12	498	520
3	1	12	221	216
-9	1	13	129	-132
-7	1	13	157	-144
-2	1	13	258	-259
3	1	13	203	202
0	1	14	166	-139
-13	2	0	249	-230
-10	2	0	212	200
-8	2	0	193	185
-5	2	0	921	904
-4	2	0	341	316
-3	2	0	682	-678
-2	2	0	700	-693
-1	2	0	415	355 *
0	2	0	350	-351
-12	2	1	129	-128
-11	2	1	184	-174
-10	2	1	203	-191
-9	2	1	129	120
-7	2	1	157	146
-6	2	1	157	143
-5	2	1	276	244
-3	2	1	673	671
-2	2	1	230	-191
-1	2	1	415	410
0	2	1	1456	1370
1	2	1	175	-189
2	2	1	516	495
3	2	1	912	-867
4	2	1	875	-852
5	2	1	286	-280
6	2	1	46	84 *
7	2	1	111	-109
10	2	1	249	-251
13	2	1	166	168
-13	2	2	221	-212
-11	2	2	193	225
-10	2	2	101	65 *
-9	2	2	313	-316
-8	2	2	203	-205
-7	2	2	488	-499
-6	2	2	221	210
-5	2	2	332	326
-4	2	2	249	243
-3	2	2	405	-393
-2	2	2	774	-731
-1	2	2	1124	1119
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2	2	2	221	211
3	2	2	534	539
4	2	2	175	-161
5	2	2	369	-375
6	2	2	479	-491
7	2	2	249	247
8	2	2	184	211
9	2	2	267	-268
10	2	2	138	-153
11	2	2	240	-230
-11	2	3	230	228
-10	2	3	138	128
-9	2	3	304	313
-8	2	3	313	-317
-7	2	3	184	-179
-6	2	3	378	-393
-5	2	3	138	141
-3	2	3	479	474
-2	2	3	230	198
-1	2	3	1483	-1332
0	2	3	286	298
1	2	3	415	-398
2	2	3	295	-280
3	2	3	129	138
4	2	3	286	291
5	2	3	166	169
6	2	3	571	572
8	2	3	295	-297
9	2	3	55	130 *
10	2	3	157	-184
-12	2	4	304	-316
-11	2	4	350	376
-9	2	4	470	-467
-6	2	4	240	243
-5	2	4	461	453
-4	2	4	230	230
-3	2	4	1014	-1011
-2	2	4	157	-130 *
-1	2	4	313	-303
0	2	4	286	290
1	2	4	74	-96 *
2	2	4	719	-712
3	2	4	544	559
4	2	4	147	-140
5	2	4	46	-78 *
6	2	4	240	-215
7	2	4	359	380
8	2	4	304	339
-12	2	5	157	157
-10	2	5	175	186
-9	2	5	267	-255
-7	2	5	258	-256
-6	2	5	433	423
-4	2	5	267	-289
-3	2	5	313	303
-2	2	5	931	-914
-1	2	5	230	-201
1	2	5	663	665
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0	6	10	166	-160
-4	6	11	175	176
-3	6	11	83	95
-4	6	12	74	108
0	6	13	175	149
-11	7	0	258	230
-9	7	0	74	-97
-7	7	0	276	239
-5	7	0	147	-153
-4	7	0	221	208
-1	7	0	138	-215 *
-8	7	1	129	125
-7	7	1	138	-136
-6	7	1	166	160
-4	7	1	111	-106
0	7	1	92	90
1	7	1	83	86
2	7	1	405	-459
4	7	1	184	-145
6	7	1	138	132
-9	7	2	240	-225
-7	7	2	369	374
-4	7	2	74	104
-3	7	2	304	260 *
-2	7	2	304	-322
0	7	2	92	-88
1	7	2	147	-142
2	7	2	157	197 *
3	7	2	55	-80 *
5	7	2	184	-196
9	7	2	193	-168
11	7	2	212	201
-6	7	3	212	198
-3	7	3	111	-99
-2	7	3	203	221
0	7	3	92	106
2	7	3	120	-122
3	7	3	55	-69
4	7	3	111	99
8	7	3	184	-196
-9	7	4	166	-173
-7	7	4	286	278
-5	7	4	341	-348
-3	7	4	111	113
-1	7	4	166	162
0	7	4	258	257
1	7	4	92	94
4	7	4	120	-103
9	7	4	166	-157
-6	7	5	111	105
-4	7	5	295	-315
-2	7	5	101	109
5	7	5	111	107
-5	7	6	322	-319
-3	7	6	212	235
-1	7	6	147	-132
2	7	6	166	-156
5	7	6	175	151
6	7	6	83	96
-7	7	7	129	111
-6	7	7	129	120
-5	7	7	120	104
-4	7	7	230	-235
-2	7	7	55	93
0	7	7	230	-202
5	7	7	83	-88
-7	7	8	157	136
-3	7	8	184	193
-1	7	8	286	-285
0	7	8	138	123
-5	7	9	138	-133
-2	7	9	286	273
0	7	9	175	-145
6	7	9	193	-164
-3	7	10	240	234
-2	7	11	166	143

Table 4. *Intramolecular distances and angles*

The estimated standard deviations in units of the last decimal position are given in parentheses. For numbering of atoms see Fig. 1.

N(1)-P	1·584 (13) Å	N(1)-P——N(3)	115·3 (7)°
N(3)-P	1·586 (13)	N(1)-S(1)-N(2)	115·6 (7)
N(1)-S(1)	1·538 (13)	N(2)-S(2)-N(3)	114·3 (7)
N(2)-S(1)	1·577 (13)	P——N(1)-S(1)	123·5 (8)
N(2)-S(2)	1·579 (13)	S(1)—N(2)-S(2)	120·3 (8)
N(3)-S(2)	1·542 (13)	S(2)—N(3)-P	120·6 (8)
P —Cl(1)	1·960 (6)		
P —Cl(2)	1·954 (6)	Cl(1)-P——Cl(2)	104·4 (3)
S(1)-Cl(3)	2·007 (6)	Cl(3)-S(1)-O(1)	105·7 (6)
S(2)-Cl(4)	2·028 (6)	Cl(4)-S(2)-O(2)	106·3 (5)
S(1)-O(1)	1·415 (14)	N(1)-P——Cl(1)	109·2 (5)
S(2)-O(2)	1·427 (12)	N(3)-P——Cl(1)	110·6 (5)
		N(1)-P——Cl(2)	109·5 (5)
P ·····S(1)	2·749 (5)	N(3)-P——Cl(2)	107·3 (5)
P ·····S(2)	2·717 (5)	N(1)-S(1)-O(1)	114·6 (8)
S(1) ···S(2)	2·737 (5)	N(2)-S(1)-O(1)	110·2 (8)
N(1)···N(2)	2·636 (17)	N(1)-S(1)-Cl(3)	105·1 (5)
N(2)···N(3)	2·622 (17)	N(2)-S(1)-Cl(3)	104·5 (5)
N(1)···N(3)	2·678 (17)	N(2)-S(2)-O(2)	110·6 (7)
		N(3)-S(2)-O(2)	113·3 (7)
		N(2)-S(2)-Cl(4)	105·6 (5)
		N(3)-S(2)-Cl(4)	106·0 (5)

distances of 0·29 and 0·26 Å respectively from this plane. The difference in location of N(1) and N(3) relative to the plane PS(1)S(2) indicates that the molecule in the crystal does not have the symmetry *m* which may be expected for a free molecule $NPCl_2(NSOCl)_2$. Table 6 shows that the best plane through P, Cl(1), Cl(2) and N(2) is a pseudo mirror plane only. The deviation from the symmetry *m* is also reflected by the unequal values of the endocyclic angles at N(1) and N(3), 123·5 and 120·6 respectively. The arrangement of the molecules in the crystal (see below) indicates that the deviations from symmetry *m* are probably a result of intermolecular interactions.

Table 5. *Distances to the plane* PS(1)S(2)

The plane obeys the equation $0{\cdot}2787X+0{\cdot}6060Y-0{\cdot}7450Z=0{\cdot}3106$ with $X=x\sin\beta$, $Y=y$ and $Z=z+x\cos\beta$ (Å).

N(1)	−0·005 Å	Cl(3)	1·893 Å
N(2)	−0·294	Cl(4)	1·990
N(3)	−0·262	O(1)	−0·794
Cl(1)	1·686	O(2)	−0·655
Cl(2)	−1·372		

Table 6. *Distances to the 'best' plane through* P, Cl(1), Cl(2) *and* N(2)

The plane obeys the equation $0{\cdot}9373X-0{\cdot}2235Y+0{\cdot}2676Z=-2{\cdot}1417$ with $X=x\sin\beta$, $Y=y$ and $Z=z+x\cos\beta$ (Å).

P	0·0079 Å	Cl(1)	−0·0028 Å
N(1)	1·3479	Cl(2)	−0·0029
N(2)	−0·0022	Cl(3)	1·9625
N(3)	−1·3294	Cl(4)	−1·5128
S(1)	1·3884	O(1)	2·3536
S(2)	−1·3411	O(2)	−2·4674

The molecule of $NPCl_2(NSOCl)_2$ may be compared with both α-$(NSOCl)_3$ (Hazell, Wiegers & Vos, 1966) and $(NPCl_2)_3$ (Wilson & Carroll, 1960) (Table 7). As observed for α-$(NSOCl)_3$ and $(NPCl_2)_3$, the endocyclic bonds in $NPCl_2(NSOCl)_2$ are short in comparison with the 'single' N–S and N–P bonds in H_3NSO_3 (1·76 Å, Sass, 1960) and $H_3NPO_3^-$ (1·77 Å, Cruickshank, 1964) respectively. This shortening has been ascribed to d_π–p_π overlap of sulphur (phosphorus) *d* orbitals and nitrogen *p* (sp^2) orbitals (Craig & Paddock, 1962; Cruickshank, 1961 *b*). As a result of this overlap double bonds are formed which may be delocalized according to the resonance scheme:

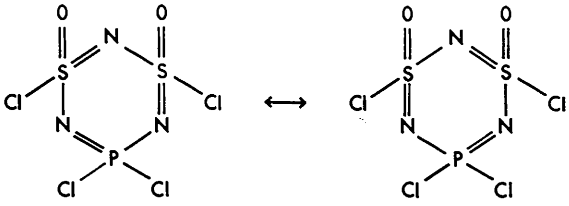


Table 7. *Conformations and bond lengths* (*in* Å) *for* α-$(NSOCl)_3$ *and* $(NPCl_2)_3$

Standard deviations for bond lengths in units of the last decimal position are given in parentheses.

Ring conformation	α-$(NSOCl)_3$ chair shaped	$(NPCl_2)_3$ planar
N–P	—	1·59 (2)
N–S	1·571 (4)	—
P–Cl	—	1·98 (1)
S–Cl	2·003 (3)	—
S–O	1·407 (7)	—

However, unlike $(NPCl_2)_3$ and α-$(NSOCl)_3$, in $NPCl_2(NSOCl)_2$ delocalization does not seem to be complete as may be seen from the N–S bond lengths. Whereas the chemically equivalent N–S bonds have equal length, 1·540 Å on average for N(1)–S(1) and

N(3)–S(2) and 1·578 Å for N(2)–S(1) and N(2)–S(2), small differences, 0·038 Å on average, occur between chemically non-equivalent N–S bonds. This may be due to the fact that the contribution of the sulphur and phosphorus *d* orbitals to the π bonding in the ring is slightly different. The same phenomenon, delocalization of the double bonds with small variations in bond lengths, has been found in the molecules $NP(C_6H_5)_2(NPCl_2)_2$ and $[NP(C_6H_5)_2]_2NPCl_2$ (Mani, Ahmed & Barnes, 1965, 1966). The N–P bond lengths in these molecules are shown in Fig. 3. The sequence of the N–P bond lengths in molecule III (Fig. 3.) may be explained as follows. The stronger electronegativity of the chlorine ligands makes the orbitals of the phosphorus atom of the PCl_2–groups more suitable for d_π–p_π bonding in the ring than those of the $P(C_6H_5)_2$–groups (Craig & Magnusson, 1956). Therefore the N–PCl_2 bonds are expected to be shorter than the N–$P(C_6H_5)_2$ bonds. Furthermore in the group Cl_2P–N–$P(C_6H_5)_2$ the p_π electron and the sp^2 lone pair electrons are more involved in the N–PCl_2 bond than in the N–$P(C_6H_5)_2$ bond. Due to this the double bond character of the former bond will increase at the cost of the double bond character of the latter. It may thus be understood that in molecule III the bonds N–$P(C_6H_5)_2$ are the largest, whereas the N–PCl_2 bonds of the uniformly substituted group Cl_2P–N–PCl_2 are larger than the other N–PCl_2 bonds.

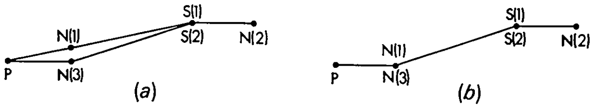


Fig. 2. Side view of the six-membered ring (*a*) as observed in $NPCl_2(NSOCl)_2$ and (*b*) the same ring in the undistorted chair conformation.

By the same reasoning the sequence of the N–P bond lengths in molecule IV can be explained. Comparison of the three molecules in Fig. 3 shows that the sequence of the lengths of the N–S bonds in $NPCl_2(NSOCl)_2$ (II) is analogous to that of N–PCl_2 in III. This suggests that in $NPCl_2(NSOCl)_2$ the *d* orbitals of sulphur are more suitable for d_π–p_π bonding in the ring than the *d* orbitals of phosporus. The relatively small value of the angle N–P–N at PCl_2 in II, in comparison with the value of 120° in the uniformly substituted N–P ring compounds, supports the view that the double bond character of the N–P bonds in II is relatively small.

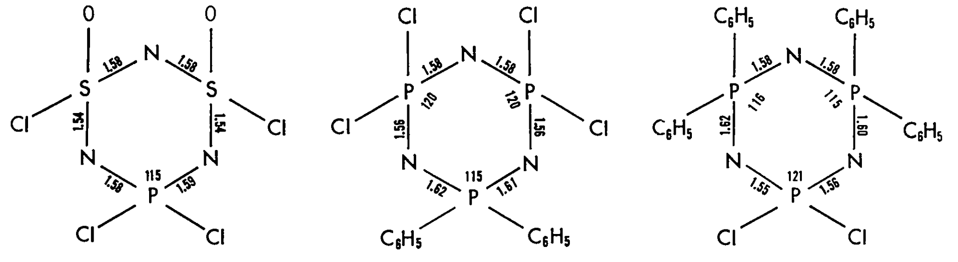
Arrangement of the molecules

Fig. 4 shows that the molecules are arranged in planes parallel to (101). The shortest intermolecular distances are observed between O(2′) and the chlorine atoms Cl(2) and Cl(3) of the neighbouring molecules. These Cl···O distances are on average 0·13 Å shorter than the sum of the van der Waals radii. It may be noticed that the bond S(2′)–O(2′) lies almost in the plane through Cl(2′) O(2′) and Cl(3) and bisects the angle Cl(2)···O(2′)··· Cl(3) (Fig. 5), the angles S(2′)–O(2′)···Cl(2) and S(2′)–O(2′)···Cl(3) being 109·9° and 111·7° respectively. This suggests that the lone pairs of oxygen atoms are involved in the intermolecular interaction. It is rea-

Table 8. *Comparison of U_{ij}(calc) and U_{ij}(obs) based on the T_{ii} and ω_{ii} values of Table* 9

The differences U_{ij}(calc)–U_{ij}(obs) are listed (in 10^{-4} Å^2) relative to the directions **a***, **b** and **c**. The standard deviations in parentheses are those of U_{ij}(obs).

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{31}$
P	39 (9)	−6 (10)	−21 (9)	1 (16)	64 (16)	9 (14)
N(1)	−66 (32)	−47 (39)	−91 (35)	−51 (55)	229 (55)	105 (54)
N(2)	70 (34)	9 (34)	15 (33)	−177 (54)	123 (53)	158 (54)
N(3)	2 (30)	−65 (40)	−64 (31)	87 (55)	256 (55)	97 (49)
S(1)	21 (8)	22 (10)	67 (8)	6 (16)	−32 (16)	13 (13)
S(2)	2 (9)	21 (10)	66 (8)	−5 (16)	110 (15)	42 (13)
Cl(1)	−53 (16)	−41 (12)	−172 (18)	−1 (22)	−94 (23)	−205 (28)
Cl(2)	1 (14)	102 (15)	−19 (10)	64 (23)	79 (19)	57 (19)
Cl(3)	9 (11)	−62 (16)	−37 (9)	−75 (22)	−245 (21)	−69 (16)
Cl(4)	−102 (11)	−68 (15)	−134 (14)	14 (22)	−176 (23)	−88 (21)
O(1)	23 (32)	−14 (49)	1 (41)	−151 (61)	−148 (71)	93 (57)
O(2)	73 (33)	39 (35)	138 (30)	237 (55)	119 (55)	201 (53)



II III IV

Fig. 3. Comparison of the molecules $NPCl_2(NSOCl)_2$ (II), $NP(C_6H_5)_2(NPCl_2)_2$ (III) and $[NP(C_6H_5)_2]_2NPCl_2$ (IV).

sonable to assume that the strong Cl···O interactions cause the deviations from symmetry *m*, which are observed for the molecule in the crystalline state.

Thermal motion

The translation tensor **T** and the libration tensor **ω** which gave the best least-squares agreement between corresponding U_{ij}(calc) and U_{ij}(obs) values were calculated according to Cruickshank's (1956) method. Comparison of the U_{ij}(calc) and U_{ij}(obs) values in Table 8 shows that the molecule cannot be considered as a rigid body performing translations and librations about its centre of mass. Especially for the atoms Cl(1) and Cl(4), the observed thermal parameters are larger than the calculated ones. This may indicate that in the P–Cl and S–Cl bonds internal (deformation) vibrations take place. The fact that, relative to the calculated U_{ij} values, the thermal motion is smaller for Cl(2) and Cl(3) than for Cl(1) and Cl(4) may be attributed to the strong Cl···O interaction described above.

Although the molecule cannot be described as a rigid body a rough impression of its thermal movement could be obtained. The magnitudes and directions of the principal axes of the **T** and **ω** tensors are given in Table 9. It may be seen that translation is smallest in a direction almost perpendicular to the plane PS(1)S(2).

Table 9. *The values of T_{ii} along, and ω_{ii} about, the principal axes*

The angles between the principal axes and the directions **a***, **b** and **c** are α, β and γ respectively; δ is the angle with the plane PS(1)S(2).

	T_{ii} (in 10^{-3} Å^2)	α(°)	β(°)	γ(°)	δ(°)
	21	102	125	38	85
Translation	30	155	66	86	3
	33	68	45	52	4
	ω_{ii} [in (°)^2]	α(°)	β(°)	γ(°)	δ(°)
	9·2	59	35	77	28
Libration	18·4	145	56	98	12
	22·0	104	97	16	59

Calculations were done at the Groningen University Computing Centre. The least-squares analysis was partly carried out by Dr J.S. Rollett in Oxford. We thank Professor E.H. Wiebenga for his interest during the course of this investigation and Drs R. Olthof-Hazekamp for programming the calculations.

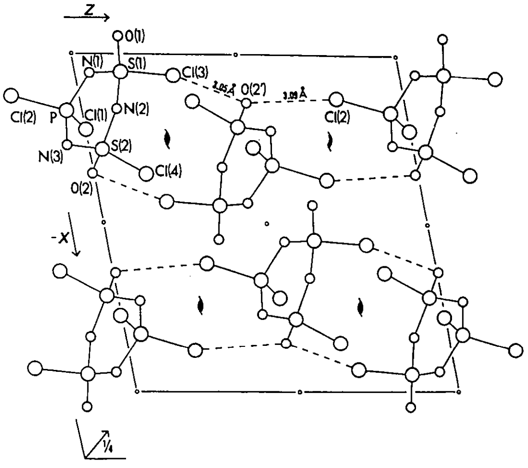


Fig. 4. Projection of the structure of $NPCl_2(NSOCl)_2$ along the *b* axis.

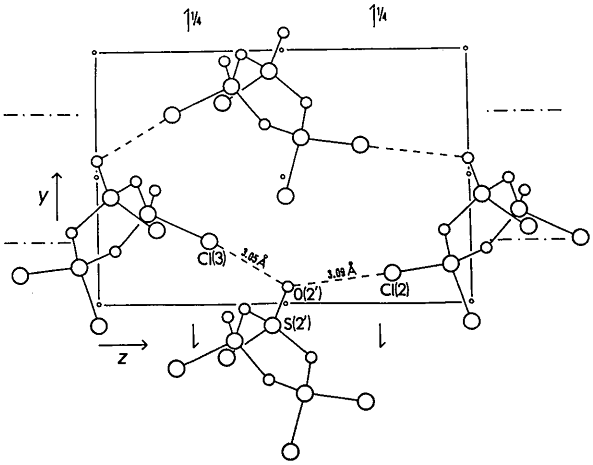


Fig. 5. Part of the structure of $NPCl_2(NSOCl)_2$ projected along [100] on to the plane (100).

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