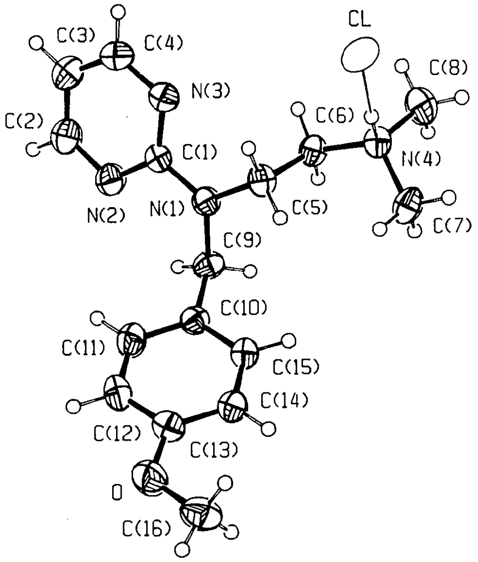

Fig. 1. An *ORTEP* (Johnson, 1976) view of thonzylamine hydrochloride with crystallographic numbering scheme.

C—C distances range between 1·373 (3) and 1·402 (3) Å [mean 1·386 (3) Å]. The N(1)—C(5) and N(1)—C(9) distances [1·457 and 1·455 (3) Å, respectively] are equal but significantly shorter than the N—C distances involving the N(4) atom which range between 1·487–1·495 (3) Å [mean 1·491 (3) Å]. A comparison of the angles around N(1) [120·1 (2), 122·2 (2) and 117·3 (2)°] and N(4) [112·8 (2), 109·7 (2) and 109·6 (2)°] clearly suggests that the two N atoms are different from each other and that N(1) is sp^2 hybridized while N(4) is sp^3 hybridized. Similar structural features have been reported in the structures of 2-{*N*-[2-(dimethylamino)ethyl]-2-thenylamino}pyridine hydrochloride (Clark & Palenik, 1972) and tripelennamine hydrochloride (Parvez, 1987). The rest of the molecular dimensions are in good agreement with the values found in other organic structures.

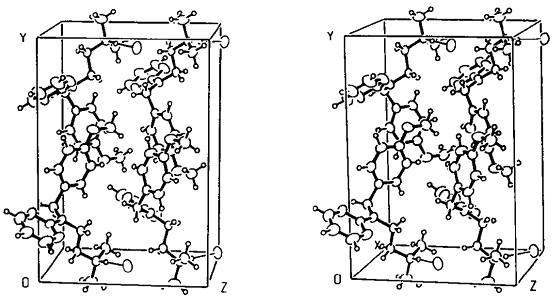

Fig. 2. A stereoview of the unit cell showing molecular packing.

The crystal structure consists of the cation containing an H atom on the dimethylamino group [H(N4)] which forms a relatively strong hydrogen bond to the anion, Cl⁻. The distances N(4)···Cl and H(N4)···Cl are 3·031 (2) and 2·08 Å, respectively, and the Cl···H(N4)—N(4) angle is 176·8°. There are no unusual intermolecular distances less than van der Waals distances and the crystal is composed of hydrogen-bonded cation–anion species (Fig. 2).

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1-Phosphabicyclo[3.3.1]nonane 1-Sulfide

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Abstract. $C_8H_{15}PS$, $M_r = 174·2$, monoclinic, $P2_1/c$, $a = 7·270\ (1)$, $b = 12·350\ (3)$, $c = 10·275\ (2)$ Å, $\beta = 98·60\ (1)°$, $V = 912·1\ (3)$ Å^3, $Z = 4$, $D_x = 1·27$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, μ(Mo $K\alpha$) = 0·403 mm^{-1}, $F(000) = 376$, $T = 293$ K, final $R = 0·032$ for 1163 observed reflections. The title compound adopts a chair–chair conformation in the solid state with the central three-atom plane as a (non-

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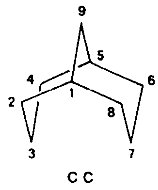
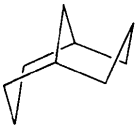
crystallographic) mirror plane. The phosphorinane rings are flattened by the repulsive interactions between their *endo*-methylene groups which exhibit a C···C transannular separation of 3·206 (4) Å.

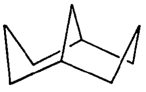
Introduction. The bicyclo[3.3.1]nonane system is of considerable interest from both synthetic and stereochemical points of view. It may be thought of as connected by the 1,3-fusion of two cyclohexane rings and consequently three conformations, chair–chair (CC), boat–chair (BC) and boat–boat (BB) are possible for the fused system.



CC



BC



BB

Several molecular mechanics calculations and recently also an *ab initio* study (Skancke, 1987) have established that the CC conformation is the preferred one for the unsubstituted hydrocarbon bicyclic system and the energies of the other forms relative to CC are of about 10 (BC) and 45 kJ mol^{-1} (BB) respectively. The predominance of the CC conformer in the gas phase (*ca* 95% at 338 K, *ca* 75% at 673 K) has been demonstrated by electron diffraction studies (Mastryukov, Popik, Dorofeeva, Golubinskii, Vilkov, Belikova & Allinger, 1981). For the crystalline state a series of X-ray studies have shown that molecules without *endo*-substituents at positions 3 and 7 generally adopt a CC conformation. However, bulky substituents at positions 3 and/or 7 can cause the existence of BC conformers. The stabilization of the BC conformation in 9-oxa-3,7-dithiabicyclo[3.3.1]nonane lacking an *endo*-substituent but with bulky heteroatoms in 3- and 7-positions has been ascribed to the lone-pair repulsions (beside steric and dipole repulsion) between the S atoms in the case of a CC conformation (Zefirov, Rogozina, Kurkutova, Goncharov & Belov, 1974). Hitherto comparably little attention has been paid to the influence of non-C atoms in 1- and/or 5-positions of the bicyclononane system upon its conformational behaviour. 3,7-Diacetyl-1,3,5,7-tetraazabicyclo[3.3.1]nonane (Choi, Santaro & Abel, 1976) and 3,7-dinitro-1,3,5,7-tetraazabicyclo[3.3.1]nonane (Choi & Bulusu, 1974) adopt CC conformations whereas the BC conformation observed for the bridgehead amide 5-phenyl-1-azabicyclo[3.3.1.]nonan-2-one is required for an effective *p*–π-overlap (Buchanan, Kitson, Mallinson, Sim, White & Cox, 1983).

Referring to our earlier X-ray studies of the dimorphic 1,5-diphosphabicyclo[3.3.0]octane 1,5-disulfide (Kaiser, Richter & Hartung, 1978; Hartung, Hickel, Kaiser & Richter, 1979) we present now the results of an X-ray analysis of 1-phosphabicyclo-[3.3.1]nonane 1-sulfide. The crystal structure of a closely related compound, 1,5-diphosphabicyclo-[3.3.1]nonane 1,5-disulfide, is reported in the following paper (Hartung, Baumeister, Rauch & Krech, 1988).

Experimental. The title compound was synthesized as described by Krech & Issleib (1976). A crystal of approximate size 0·43 × 0·32 × 0·26 mm mounted on a Syntex $P2_1$ diffractometer yielded lattice parameters by a least-squares refinement of the setting angles for 14 reflections (Mo $K\alpha$ radiation, graphite monochromator). 1381 unique reflection intensities were measured for $3 \leq 2\theta \leq 48°$ and h, k, l from −8, 0, 0 to 8, 14, 11. 1163 (= 84·2%) of the reflections had intensities $I \geq 1{\cdot}96\sigma(I)$ and were considered to be observed. The intensities of the check reflections varied from 30·3 (3) to 32·5 (3) × 10^4 for $2\bar{2}\bar{2}$ and from 17·3 (2) to 18·5 (2) × 10^4 for $1\bar{4}2$. Lp corrections were applied but absorption effects were ignored. The structure was solved by application of *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Full-matrix least-squares refinement on F with anisotropic thermal parameters for non-H atoms and isotropic ones for H atoms (all found in a difference electron density map) led to a final R of 0·032 (wR = 0·030). In the last stages of refinement the weighting scheme was changed from unit to counter weights with $w = 1{\cdot}506/\sigma^2(F)$. The maximum shift/e.s.d. ratio during the last least-squares cycle was 0·010. A final difference Fourier map showed maximum and minimum peaks of 0·172 and −0·219 e Å^{-3}, respectively. Data reduction and *MULTAN*80 were run on a RIAD computer of the Poznań University, all other calculations were performed on an ESER 1040 computer of the Halle University. The following programs were used: *MULTAN*80, *SHELX*76 (Sheldrick, 1976), *PRARA* (Jaskólski, 1980) and *EDIT* (Jaskólski, 1982). Atomic scattering factors were those of *SHELX*.

Discussion. Final atomic parameters are listed in Table 1.* Atomic numbering and molecular geometry can be seen from Fig. 1. Bond lengths and angles, and torsion angles defining the ring conformations, are given in Table 2.

The 1-phosphabicyclo[3.3.1]nonane 1-sulfide molecule adopts a CC conformation. Since corresponding distances and angles on opposite sides of the plane through S, P, C(7), C(8) agree well the molecule has to excellent approximation C_s symmetry. The six-

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44943 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters and equivalent isotropic temperature factors* (Å²) *for the non*-H *atoms*

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
P	0·12343 (10)	0·14975 (5)	0·65454 (7)	0·0386 (2)
S	−0·06772 (12)	0·20432 (6)	0·51545 (8)	0·0626 (3)
C(1)	0·2533 (4)	0·2575 (2)	0·7466 (3)	0·047 (1)
C(2)	0·4171 (4)	0·2194 (2)	0·8459 (3)	0·049 (1)
C(3)	0·5404 (4)	0·1343 (3)	0·7944 (3)	0·052 (1)
C(4)	0·3462 (5)	−0·0409 (2)	0·8129 (3)	0·052 (1)
C(5)	0·1787 (4)	0·0037 (2)	0·8695 (3)	0·047 (1)
C(6)	0·0334 (4)	0·0588 (3)	0·7679 (3)	0·050 (1)
C(7)	0·3064 (4)	0·0698 (2)	0·6034 (3)	0·046 (1)
C(8)	0·4425 (4)	0·0351 (2)	0·7255 (3)	0·047 (1)

Table 2. *Bond lengths* (Å), *angles* (°) *and torsion angles* (°)

P–S	1·958 (1)	C(3)–C(8)	1·535 (4)
P–C(1)	1·814 (3)	C(4)–C(5)	1·528 (4)
P–C(6)	1·809 (3)	C(4)–C(8)	1·536 (4)
P–C(7)	1·797 (3)	C(5)–C(6)	1·529 (4)
C(1)–C(2)	1·522 (4)	C(7)–C(8)	1·538 (4)
C(2)–C(3)	1·526 (4)		

S–P–C(1)	112·7 (1)	C(2)–C(3)–C(8)	116·9 (2)
S–P–C(6)	113·5 (1)	C(8)–C(4)–C(5)	117·5 (2)
S–P–C(7)	116·8 (1)	C(4)–C(5)–C(6)	114·1 (2)
C(1)–P–C(6)	109·3 (1)	P–C(6)–C(5)	115·9 (2)
C(1)–P–C(7)	101·8 (1)	P–C(7)–C(8)	109·2 (2)
C(6)–P–C(7)	101·6 (1)	C(3)–C(8)–C(4)	116·0 (2)
P–C(1)–C(2)	114·6 (2)	C(3)–C(8)–C(7)	110·5 (2)
C(1)–C(2)–C(3)	115·0 (2)	C(4)–C(8)–C(7)	110·7 (2)

S–P–C(1)–C(2)	−173·7 (2)	P–C(1)–C(2)–C(3)	45·8 (3)
C(6)–P–C(1)–C(2)	59·3 (2)	C(1)–C(2)–C(3)–C(8)	−50·4 (3)
C(7)–P–C(1)–C(2)	−47·7 (2)	C(2)–C(3)–C(8)–C(4)	−66·2 (3)
S–P–C(6)–C(5)	173·5 (2)	C(2)–C(3)–C(8)–C(7)	60·8 (3)
C(1)–P–C(6)–C(5)	−59·9 (2)	C(8)–C(4)–C(5)–C(6)	49·1 (3)
C(7)–P–C(6)–C(5)	47·2 (2)	C(5)–C(4)–C(8)–C(3)	66·1 (3)
S–P–C(7)–C(8)	179·7 (2)	C(5)–C(4)–C(8)–C(7)	−60·8 (3)
C(1)–P–C(7)–C(8)	56·5 (2)	C(4)–C(5)–C(6)–P	−44·5 (3)
C(6)–P–C(7)–C(8)	−56·2 (2)	P–C(7)–C(8)–C(3)	−64·9 (3)
		P–C(7)–C(8)–C(4)	65·0 (3)

membered rings *A* [built up of atoms P, C(1), C(2), C(3), C(8), C(7)] and *B* [P, C(7), C(8), C(4), C(5), C(6)] deviate distinctly from the ideal chair conformation. Their endocyclic torsion angles range from 45·8 to 64·9° (mean 54·3°) for ring *A* and from 44·5 to 65·0° (mean 53·8°) for ring *B*. But ideal geometry for a cyclohexane ring, in the chair form, would have all torsion angles with an absolute magnitude of 56° (Altona & Sundaralingam, 1970). The observed deviations arise for the following two reasons. First, as a result of the greater length of the C–P bond compared with the C–C bond, the phosphorinane ring is flattened around the P atom. Second, owing to steric repulsion between the *endo* hydrogens at C(2) and C(5) both 'wings' of the phosphabicyclononane skeleton [P, C(1)...C(3), C(8), and C(8), C(4)...C(6), P] are flattened compared with simple cyclohexane systems. This fact is expressed by the corresponding torsion angles (Table 2) but it can also be visualized in terms of least-squares planes. The deviations of atoms C(2) and C(7) from the best plane through P, C(1), C(3), C(8) (plane I) and of C(5) and C(7) from the best plane through P, C(8), C(4), C(6) (plane II) should have the same absolute value of 0·73 Å (Bhattacharjee & Chacko, 1979). In reality the deviations of atoms C(2) and C(5) from planes I and II are −0·539 (3) and −0·532 (3) Å, respectively, while atom C(7) deviates from these planes by the significantly larger distances of 0·783 (3) and 0·782 (3) Å, respectively. The angle between planes I and II is 112°. The transannular C(2)···C(5) separation of 3·206 (4) Å is in good agreement with X-ray results for related compounds [*e.g.* 3·134 (3) Å in 9-cyclohexylbicyclo[3.3.1]nonan-9-ol (Sim, 1983)] and is only a little longer than the value of 3·06 Å obtained in an electron diffraction study of bicyclo[3.3.1]nonane (Mastryukov, Osina, Dorofeeva, Popik, Vilkov & Belikova, 1979). Also the non-bonded distance between the *endo* hydrogen atoms H(21)···H(52), being 2·00 (4) Å, is in the expected range.

The observed bond lengths and angles agree well with corresponding values reported in the literature. This is true for individual as well as mean values [$\overline{\mathrm{C{-}C}}$ = 1·530 (5), $\overline{\mathrm{C{-}P}}$ = 1·807 (7) Å]. The P–S bond length of 1·958 (1) Å is within the range given by a compilation of related compounds in an earlier paper (Kaiser, Richter & Hartung, 1978).

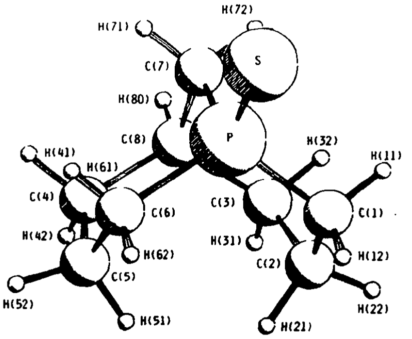

Fig. 1. Molecular structure of the title compound.

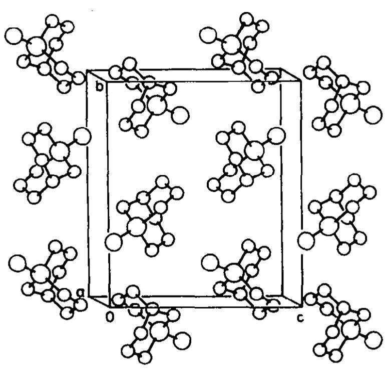

Fig. 2. Crystal structure of the title compound.

The crystal packing is illustrated in Fig. 2. The molecules are held together by normal van der Waals interactions. No intermolecular contact is shorter than the sum of the appropriate van der Waals radii.

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1,5-Diphosphabicyclo[3.3.1]nonane 1,5-Disulfide

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Abstract. $C_7H_{14}P_2S_2$, $M_r = 224\cdot2$, monoclinic, $P2_1/c$, $a = 11\cdot021\,(2)$, $b = 8\cdot055\,(1)$, $c = 12\cdot195\,(3)$ Å, $\beta = 90\cdot50\,(2)°$, $V = 1082\cdot6\,(4)$ Å^3, $Z = 4$, $D_m = 1\cdot36$ (flotation in aqueous KI solution), $D_x = 1\cdot38$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0\cdot71069$ Å, $\mu = 0\cdot66$ mm^{-1}, $F(000) = 472$, $T = 293$ K, final $R = 0\cdot032$ ($wR = 0\cdot030$) for 1224 observed reflections. The 1,5-diphosphabicyclo[3.3.1]nonane 1,5-disulfide molecule has a chair–chair conformation and (in very good approximation) C_{2v} (*mm*) symmetry. The strong repulsion between the *endo*-methylene groups is reflected in the transannular C···C distance of 3·296 (4) Å and causes a marked flattening of the diphosphorinane rings.

Introduction. Recently the bicyclo[3.3.1]nonane system has been the subject of much theoretical and experimental work showing its relevance to chemical synthesis and stereochemistry. In the preceding paper (Baumeister, Hartung & Krech, 1988) we report the results of an X-ray analysis of 1-phosphabicyclo[3.3.1]nonane 1-sulfide. The main interest in the molecular structure of this compound was directed to the substitution of one bridgehead C atom by a P atom and its influence on the stereochemistry of the bicyclic skeleton. We now present the crystal structure of the closely related compound 1,5-diphosphabicyclo[3.3.1]nonane 1,5-disulfide in which both bridgehead positions are occupied by P atoms.

Experimental. 1,5-Diphosphabicyclo[3.3.1]nonane 1,5-disulfide was first synthesized by Krech (1985). A crystal with dimensions $0\cdot22 \times 0\cdot31 \times 0\cdot35$ mm was investigated on a Syntex $P2_1$ diffractometer using graphite-monochromatized Mo $K\alpha$ radiation. Lattice parameters were derived from least-squares refinement of the setting angles of 15 reflections. Intensities for 1595 unique reflections with $2 \le 2\theta \le 48°$ were measured in the h,k,l range $\overline{12}$,0,0 to 12,9,13, 1224 with $I \ge 1\cdot96\sigma(I)$ were considered to be observed. The check reflection intensities varied from $4\cdot44\,(5)$ to $4\cdot57\,(5) \times 10^4$ (=2·8%) for $\overline{1}35$ and from $10\cdot9\,(1)$ to $11\cdot5\,(1) \times 10^4$ (=4·9%) for $\overline{2}33$. The structure was solved by standard Patterson and Fourier techniques and refined (on F) by full-matrix least squares with anisotropic thermal parameters for the non-H atoms

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