The results of the molecular-mechanics analysis compare well with the experimental structure, taking into account that the potential-energy function applied was fitted to gas-phase data. The central C—C and the C=N bond lengths show therefore some deviation. The distortion of the *tert*-butyl groups as reflected in the C—C—C angles is well calculated.

We thank D. J. Stufkens of the University of Amsterdam for providing the crystals.

Cooperation with K. Rasmussen of the Technical University of Denmark (Lyngby) is gratefully acknowledged.

The investigations were supported in part (ALS) by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Advancement of Pure Research (ZWO).

References

Boer, J. L. de & Duisenberg, A. J. M. (1984). *Acta Cryst.* A**40**, C410.
Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.
Exner, O. & Kliegman, J. M. (1971). *J. Org. Chem.* **36**, 2014–2015.
Fernholt, L., Rømming, C. & Samdal, S. (1981). *Acta Chem. Scand. Ser. A*, **35**, 707–715.
Graham, A. J., Akrigg, D. & Sheldrick, B. (1983). *Acta Cryst.* C**39**, 192–194.
Hargittai, I. & Seip, R. (1976). *Acta Chem. Scand. Ser. A*, **30**, 540–546.
Huige, C. J. M. (1984). Thesis, Univ. of Utrecht. To be published.
Jeffrey, G. A., Ruble, J. R. & Pople, J. A. (1982). *Acta Cryst.* B**38**, 1975–1980.
Keijsper, J., van der Poel, H., Polm, L. H., van Koten, G., Vrieze, K., Seignette, P. F. A. B., Varenhorst, R. & Stam, C. (1983). *Polyhedron*, **2**, 1111–1116.
Kliegman, J. M. & Barnes, R. K. (1970). *Tetrahedron*, **26**, 2555–2560.
Kveseth, K., Seip, R. & Kohl, D. A. (1980). *Acta Chem. Scand. Ser. A*, **34**, 31–42.
Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN*80. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
Mugnoli, A. & Simonetta, M. (1976). *J. Chem. Soc. Perkin Trans.* 2, pp. 1831–1835.
Niketic, S. R. & Rasmussen, K. (1977). *The Consistent Force Field: A Documentation*. In *Lecture Notes in Chemistry*, Vol. 3. Heidelberg: Springer Verlag.
Rasmussen, K. (1983). *J. Mol. Struct.* **97**, 53–56.
Sheldrick, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.
Spek, A. L. (1982). *The EUCLID package*. In *Computational Crystallography*, edited by D. Sayre, p. 528. Oxford: Clarendon Press.

Acta Cryst. (1985). C**41**, 116–119

Structures of Inorganic Rings as Antitumor Agents. IV.* Structure of 1,3,3,5,5-Pentakis(1-aziridinyl)-1λ^6,2,4,6,3λ^5,5λ^5-thiatriazadiphosphorine 1-Oxide Monohydrate, $C_{10}H_{20}N_8OP_2S.H_2O$

By Jean Galy† and Renée Enjalbert

Laboratoire de Chimie de Coordination du CNRS, 205 *route de Narbonne,* 31400 *Toulouse CEDEX, France*

and Jean-François Labarre

Laboratoire Structure et Vie, Université Paul Sabatier, 118 *route de Narbonne,* 31062 *Toulouse CEDEX, France*

(*Received* 6 *February* 1984; *accepted* 20 *September* 1984)

Abstract. $M_r = 380$, monoclinic, Pn, $a = 8.440$ (9), $b = 8.037$ (5), $c = 12.81$ (1) Å, $\beta = 92.87$ (6)°, $V = 868$ (1) Å^3, $Z = 2$, $D_x = 1.385$ (5), $D_m = 1.37$ (4) Mg m^{-3}, λ(Mo $K\bar{\alpha}$) = 0.71069 Å, $\mu = 0.34$ mm^{-1}, $F(000) = 400$, $T = 293$ K. Final $R = 0.039$ for 1907 unique observed reflections. The crystal structure consists of $N_3P_2SO(NC_2H_4)_5$ entities associated with one H_2O molecule. The vicinity of H_2O and cyclophosphazenic molecules induces a disorder both of the O atom and of the aziridinyl group fixed on the S atom of the N_3P_2S ring. The two new conformations exhibited by this molecule are one more example of its outstanding versatility.

Introduction. Some thiatriazadiphosphorines belonging to the $(NPaz_2)_2(NSOX)$ family with X = F, phenyl, or aziridinyl (az) have proved to exhibit a remarkable antitumor activity (Labarre, 1982).

* Part III: Cameron, Labarre & Graffeuil (1982).
† Author to whom correspondence should be addressed.

0108-2701/85/010116-04$01.50

The compound 1,3,3,5,5-pentakis(1-aziridinyl)-1λ^6,-2,4,6,3λ^5,5λ^5-thiatriazadiphosphorine 1-oxide, $\{NP[N(CH_2)_2]_2\}_2[NSON(CH_2)_2]$, named SOaz for convenience, exhibits two allotropic varieties, the former crystallizing in the orthorhombic system, *i.e.* SOaz(I), the latter in the monoclinic system, *i.e.* SOaz(II). The outstanding feature, emphasized by a thorough crystallographic study (Galy, Enjalbert, van der Huizen, van de Grampel & Labarre, 1981), is the conformations adopted by this molecule which are quite different for the unique molecule of SOaz(I) and for the two crystallographically independent molecules of SOaz(II), namely SOaz(II*A*) and SOaz(II*B*), where the settings of the aziridinyl ligands drastically differ from each other. A further allotropic variety exists at 'high' temperature, named SOaz(III) (Galy & Enjalbert, 1980, unpublished results), which has been characterized by the powder diffraction method.

When injected as a medication, SOaz(II) produced as a powder is dissolved in physiological serum. It is highly soluble (0·45 g L^{-1}). It would be of great importance to know the exact conformation of SOaz when injected as an antitumor drug. With this aim, one of us (RE) started growing crystals of SOaz from a water solution. Single crystals were finally obtained after gentle evaporation of the solution for five weeks. The crystallographic analysis revealed a new moiety, the SOaz monohydrate, $(NPaz_2)_2(NSOaz).H_2O$, conveniently named hereafter SOaz(*W*).

Experimental. Colorless block, trigonal prism form ($h = 0·4$ mm, $r_{basis} = 0·3$ mm), CAD-4 Nonius diffractometer, graphite-monochromated Mo $K\alpha$; take-off angle = 2·5°; 25 reflections with $3 < \theta < 20°$ used for measuring lattice parameters; space group (identified by precession method) verified by rapid measurement of $h0l$, $hk0$ and $0kl$ reflections to check the rotation $h0l$, $h + l = 2n$, implying $P2/n$ or Pn space group. For data collection $\theta_{max} = 30°$; θ–2θ scan with $\Delta\theta$ scan = 1·1° + 0·35° tanθ, prescan speed = 10° min^{-1}. $\sigma(I)/I$ for final scan: 0·018; max. time for final scan: 80 s; standard reflections 013, 0,0,10, 402 measured after periods of 3600 s, no significant variation during whole data collection; 1976 unique reflections measured, range of hkl: h −11→11, k 0→11, l 0→17; Lorentz and polarization factors; no absorption correction. Structure resolution and refinement: 1907 reflections with $I > 3\sigma(I)$ utilized; direct methods; full-matrix least squares (F); because of the selected space group Pn, x and z atomic coordinates fixed for one atom; anisotropic thermal parameters for all non-H atoms; H atoms in aziridinyl group positioned according to Dermer & Ham (1969), *i.e.* C—H = 0·97 Å, H—C—H = 116° and isotropic thermal parameters $U(H_i) = U_{eq}(C_i) + 0·015$ Å^2; H atoms of the water molecule not included; 242 refined variable parameters. $R = 0·0385$, $R_w = 0·0396$, $w = 1$, $S = 0·624$. Max. and

Table 1. *Positional and equivalent isotropic thermal parameters of non-*H *atoms, with their e.s.d.'s in parentheses*

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

	x	y	z	U_{eq}(Å^2)
S	0·0332 (2)	0·1649 (2)	0·6127 (1)	0·0459 (7)
P(1)	0·28†	0·3284 (1)	0·72†	0·0308 (5)
P(2)	0·2988 (2)	0·2579 (2)	0·5088 (1)	0·0332 (5)
O*A*	−0·0739 (10)	0·0434 (11)	0·6286 (6)	0·053 (5)
O*B*	0·0177 (11)	−0·0239 (10)	0·6327 (6)	0·051 (5)
W	−0·2663 (7)	−0·2204 (8)	0·6936 (4)	0·096 (4)
N(1)	0·1105 (5)	0·2366 (6)	0·7139 (3)	0·041 (2)
N(2)	0·3591 (5)	0·3520 (5)	0·6121 (3)	0·036 (2)
N(3)	0·1318 (5)	0·1679 (6)	0·5147 (3)	0·044 (2)
N(4)*A*	−0·0807 (11)	0·3507 (14)	0·5911 (7)	0·042 (5)
N(4)*B*	−0·1360 (10)	0·2104 (16)	0·5712 (8)	0·056 (6)
N(5)	0·2589 (6)	0·5022 (6)	0·7850 (4)	0·047 (2)
N(6)	0·4086 (5)	0·2325 (6)	0·8010 (3)	0·043 (2)
N(7)	0·2888 (5)	0·3819 (6)	0·4044 (3)	0·047 (3)
N(8)	0·4376 (5)	0·1270 (6)	0·4733 (4)	0·048 (3)
C(1)*A*	−0·2287 (13)	0·3236 (22)	0·5254 (10)	0·069 (8)
C(2)*A*	−0·2391 (23)	0·3633 (25)	0·6316 (16)	0·069 (11)
C(1)*B*	−0·1700 (24)	0·3835 (23)	0·5822 (14)	0·076 (11)
C(2)*B*	−0·2425 (16)	0·2640 (27)	0·6498 (13)	0·067 (9)
C(3)	0·2000 (9)	0·6560 (8)	0·7359 (6)	0·067 (4)
C(4)	0·3669 (8)	0·6419 (7)	0·7706 (6)	0·063 (4)
C(5)	0·3546 (9)	0·1541 (12)	0·8957 (6)	0·089 (5)
C(6)	0·4029 (10)	0·0506 (9)	0·8067 (7)	0·080 (5)
C(7)	0·2190 (7)	0·5461 (8)	0·4159 (5)	0·060 (4)
C(8)	0·3881 (7)	0·5316 (9)	0·4058 (5)	0·058 (4)
C(9)	0·3943 (8)	−0·0229 (9)	0·4108 (5)	0·066 (4)
C(10)	0·4441 (9)	−0·0394 (9)	0·5204 (6)	0·072 (4)

† Coordinates fixed.

Table 2. *Selected bond distances* (Å) *and angles* (°) *with their e.s.d.'s in parentheses*

P(1)—N(1)	1·608 (4)	N(1)—P(1)—N(2)	115·3 (2)
P(1)—N(2)	1·576 (4)	P(1)—N(2)—P(2)	122·8 (3)
P(2)—N(2)	1·586 (4)	N(2)—P(2)—N(3)	115·2 (2)
P(2)—N(3)	1·589 (5)	P(2)—N(3)—S	124·3 (3)
S—N(1)	1·535 (4)	N(3)—S—N(1)	117·3 (3)
S—N(3)	1·540 (4)	S—N(1)—P(1)	123·5 (3)
P(1)—N(5)	1·640 (5)	N(5)—P(1)—N(6)	99·4 (2)
N(5)—C(3)	1·463 (8)	P(1)—N(5)—C(3)	123·0 (4)
N(5)—C(4)	1·464 (8)	P(1)—N(5)—C(4)	120·3 (4)
C(3)—C(4)	1·460 (10)	C(3)—N(5)—C(4)	59·8 (4)
P(1)—N(6)	1·654 (4)	P(1)—N(6)—C(5)	120·0 (4)
N(6)—C(5)	1·460 (9)	P(1)—N(6)—C(6)	118·3 (4)
N(6)—C(6)	1·465 (8)	C(5)—N(6)—C(6)	61·0 (6)
C(5)—C(6)	1·485 (12)		
P(2)—N(7)	1·666 (5)	N(7)—P(2)—N(8)	99·7 (2)
N(7)—C(7)	1·456 (8)	P(2)—N(7)—C(7)	117·7 (4)
N(7)—C(8)	1·466 (8)	P(2)—N(7)—C(8)	118·4 (4)
C(7)—C(8)	1·445 (9)	C(7)—N(7)—C(8)	59·3 (4)
P(2)—N(8)	1·655 (5)	P(2)—N(8)—C(9)	120·4 (4)
N(8)—C(9)	1·483 (8)	P(2)—N(8)—C(10)	118·6 (4)
N(8)—C(10)	1·467 (8)	C(9)—N(8)—C(10)	58·9 (4)
C(9)—C(10)	1·451 (10)		
S—O*A*	1·353 (9)	O*A*—S—N(4)*A*	105·5 (5)
S—O*B*	1·546 (8)	O*A*—S—N(4)*B*	67·0 (6)
S—N(4)*A*	1·790 (11)	O*B*—S—N(4)*A*	142·7 (5)
S—N(4)*B*	1·542 (9)	O*B*—S—N(4)*B*	101·8 (6)
N(4)*A*—C(1)*A*	1·48 (2)	S—N(4)*A*—C(1)*A*	113·2 (9)
N(4)*A*—C(2)*A*	1·46 (2)	S—N(4)*A*—C(2)*A*	119·8 (1·0)
C(1)*A*—C(2)*A*	1·40 (3)	S—N(4)*B*—C(1)*B*	112·6 (1·0)
N(4)*B*—C(1)*B*	1·43 (2)	S—N(4)*B*—C(2)*B*	115·3 (8)
N(4)*B*—C(2)*B*	1·45 (2)		
C(1)*B*—C(2)*B*	1·45 (3)		
		C(1)*A*—N(4)*A*—C(2)*A*	56·9 (1·0)
		C(1)*B*—N(4)*B*—C(2)*B*	60·5 (1·2)

min. height in final difference synthesis +0·4 and −0·2 e Å^{-3}; $(\Delta/\sigma)_{\rm mean} = 0{\cdot}09$; atomic scattering factors corrected for anomalous dispersion from Cromer & Waber (1974). Calculations used *SHELX*76 (Sheldrick, 1976) and illustrations the *ORTEP* program (Johnson, 1965).

Discussion. Fractional coordinates and equivalent isotropic thermal parameters of non-H atoms are listed in Table 1.* Main interatomic distances and bond angles are given in Table 2.

The main feature of the structure of SOaz(*W*) is again the presence of two different conformations of the SOaz molecule, but instead of having two independent molecules perfectly ordered as in SOaz(II), SOaz(*WA*) and SOaz(*WB*) are randomly dispersed in the network. An *ORTEP* drawing (conformation *A*) is given in Fig. 1. Fig. 2 illustrates the packing of the SOaz and water molecules through the projection onto the (010) plane.

The part of the SOaz molecule closest to the water molecule is the moiety $\mathrm{S}{<}^{\mathrm{O}}_{\mathrm{az}}$ which is also the only disordered part of the molecule. The O is split on two distinct crystallographic sites (50% occupation each) just as are all the atoms of the aziridinyl moiety. Such a situation gives rise to two compatible conformations, SOaz(*WA*) and SOaz(*WB*) (Fig. 3). The dihedral angle between N(4)*A*—S—O*A* and N(4)*B*—S—O*B* alternations is 18·6°. The water molecule *W* is rather close to both *W*—O*A* and *W*—O*B*, 2·82 and 3·01 Å, implying the likely existence of hydrogen bonding. Nevertheless it has not been possible to locate the true positions for the H atoms around *W* despite the presence of four small peaks in the difference Fourier maps situated at 0·9–1·00 Å. The disorder could be related to this hydrogen-bonding interaction not adopting predominantly one arrangement or the other.

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39756 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

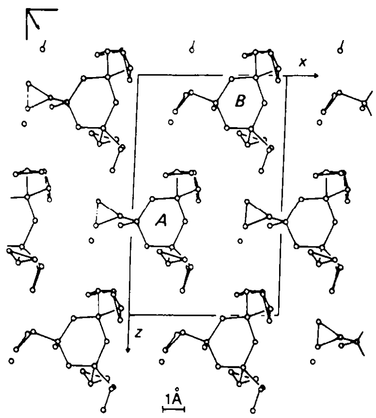

Fig. 2. Projection onto the (010) plane of the SOaz(*W*) structure (H atoms omitted). Conformations *A* and *B* have been arbitrarily chosen.

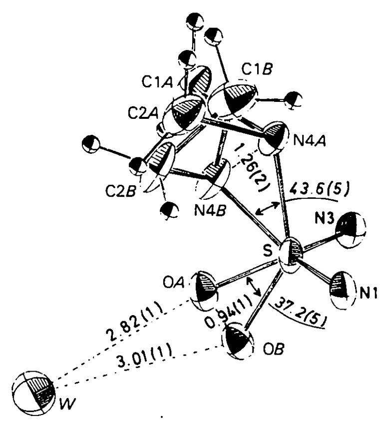

Fig. 3. Geometry around the S atom (distances in Å, angles in °).

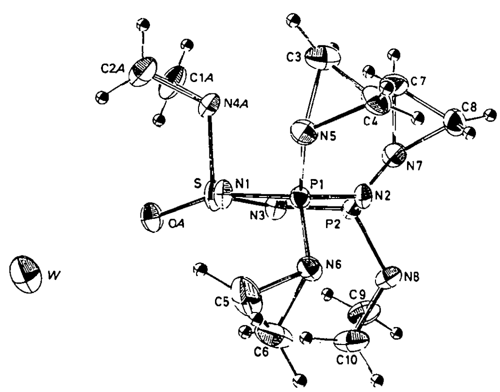

Fig. 1. Perspective view of the SOaz(*W*) molecule in conformation *A*.

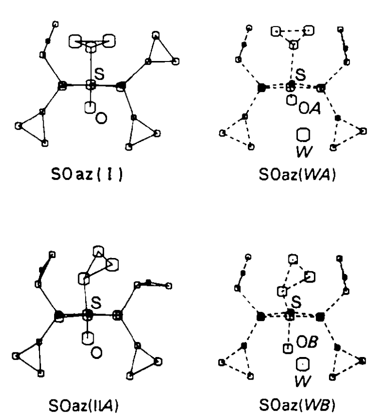

Fig. 4. Comparison of flexibilities in SOaz forms.

Both A and B conformations of the SOaz(W) molecule can be directly compared with the previous one (Galy *et al.*, 1981). Fig. 4 summarizes the extraordinary versatility of this molecule in the setting of its aziridinyl wings.

References

CAMERON, T. S., LABARRE, J.-F. & GRAFFEUIL, M. (1982). *Acta Cryst.* B**38**, 2000–2004.

CROMER, D. T. & WABER, J. T. (1974). In *International Tables for X-ray Crystallography*, Vol. IV. Birmingham: Kynoch Press.

DERMER, O. C. & HAM, G. E. (1969). In *Ethyleneimine and other Aziridines*. New York: Academic Press.

GALY, J., ENJALBERT, R., VAN DER HUIZEN, A. A., VAN DE GRAMPEL, J. C. & LABARRE, J.-F. (1981). *Acta Cryst.* B**37**, 2205–2209.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

LABARRE, J.-F. (1982). *Up-to-date Improvements in Inorganic Ring Systems as Anticancer Agents*. In *Topics in Current Chemistry*, Vol. 102, pp. 1–88. Berlin: Springer Verlag.

SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Acta Cryst. (1985). C**41**, 119–121

Structure of the 1/1·5 Complex Formed between the Bis(triphenylphosphoranediyl)ammonium cation (R^+) and 7,7,8,8-Tetracyano-*p*-quinodimethane (TCNQ), $C_{36}H_{30}NP_2^+.C_{12}H_{12}N_4^-.0{\cdot}5C_{12}H_{12}N_4.C_2H_3N$

BY JOAN HALFPENNY

Department of Applied Chemical Sciences, Napier College, Colinton Road, Edinburgh EH10 5DT, Scotland

(*Received* 9 *July* 1984; *accepted* 21 *September* 1984)

Abstract. $R^+(TCNQ)^-(TCNQ)_{0.5}.CH_3CN$, $M_r = 885$, triclinic, $P\bar{1}$, $a = 8{\cdot}84$ (1), $b = 16{\cdot}70$ (1), $c = 17{\cdot}16$ (1) Å, $\alpha = 69{\cdot}85$ (7), $\beta = 84{\cdot}11$ (9), $\gamma = 85{\cdot}26$ (9)°, $V = 2365$ (6) Å^3, $Z = 2$, $D_m = 1{\cdot}24$, $D_x = 1{\cdot}24$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 0{\cdot}105$ mm^{-1}, $F(000) = 966$, room temperature, $R = 0{\cdot}0625$, $R_w = 0{\cdot}056$ for 2833 diffractometer-measured intensities with $I > 3\sigma(I)$. The cation has the expected non-linear structure. The structural unit contains 1·5 TCNQ molecules, TCNQ(B) being at a centre of symmetry while TCNQ(A) is in a general position. The TCNQ molecules are stacked in groups of three, ABA. Within the triad the molecules are displaced so that there is overlap between the quinonoid double bond and the ring of the adjacent molecule. Individual triads are well separated without overlap. A molecule of solvent, methyl cyanide, is included in the structural unit.

Introduction. The compound was prepared as part of an investigation into the preparation of conducting and semi-conducting complexes of TCNQ with various cations (Ahmad, Bryce, Halfpenny & Weiler, 1984). Its conductivity is that of a typical semi-conductor. The compound was considered worthy of structure determination owing to the large size of the cation, which is by far the most complex in a TCNQ compound studied by X-ray diffraction.

Experimental. Initially composition of compound unknown. Accurate cell dimensions from least-squares refinement of 12 strong reflections (Mo $K\alpha$ θmin. 5, max. 17°), Enraf–Nonius CAD-4 4-circle diffractometer. Density by flotation indicated $Z = 2$. 7604 reflections measured, Stoe Stadi-2 2-circle diffractometer, graphite-monochromatized Mo $K\alpha$ radiation; crystal $0{\cdot}4 \times 0{\cdot}5 \times 0{\cdot}05$ mm, layers $h = 0$–8, $k \pm 18$, $l \pm 19$, max. $\sin\theta/\lambda = 0{\cdot}595$ Å^{-1}, separate standard for each layer measured every 10 reflections (intensity variation < 2%). 7009 unique reflections ($R_{int} = 0{\cdot}019$), 2833 with $I > 3\sigma(I)$ used for refinement. No absorption correction. Structure solved by *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined using *SHELX*76 (Sheldrick, 1976) full-matrix least squares on F magnitudes. Phenyl groups treated as rigid hexagons with C—C = 1·395 Å. Difference map showed one molecule of methyl cyanide in asymmetric unit. Hydrogen atoms, including those of methyl cyanide, introduced at calculated positions (C—H = 1·08 Å) and all H within each molecule or phenyl group given same isotropic U value. All non-H atoms except C(1), C(2), C(3), C(7), C(8), C(13), C(14), C(19), C(20), C(25), C(26), C(31) and C(32) given anisotropic U_{ij}. These exceptions were necessary on account of limited capacity of *SHELX* program [$2N$(anis.) + N(iso.) ≤ 160], the basis for exception

0108-2701/85/010119-03$01.50