approximately equal, this does not apply for the ring bond angles. It turns out that the ring puckering is mainly accomplished by the distortion of the valence angle at C(2) by 2·2 (2)° since the angle at C(3) remains approximately 90°.

As a result of the cyclobutane-ring puckering, C(1) becomes an axial substituent with an angle of 26·6 (2)° between the C(1)—C(2) bond and the normal to the least-squares plane through C(2), C(3), $C(2^{i})$ and $C(3^{i})$, whereas C(4) becomes an equatorial substituent with corresponding angle 58·3 (2)°. The observed ring puckering avoids very short H···H contacts for H atoms attached to C(4) and $C(1^{i})$ that would arise in the case of a flat ring as may be seen from space-filling models.

The authors are grateful to Dr J. Leitich for making a sample of the title compound available to them. The investigations were supported in part (ALS, PJJAT) by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

References

ALLEN, F. H. (1984). *Acta Cryst.* B**40**, 64–72.
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.
LEITICH, J. (1982). *Tetrahedron*, **38**, 1303–1309.
MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.
MORIARTY, R. M. (1974). *Topics in Stereochemistry*, Vol. 8, edited by E. L. ELIEL & N. L. ALLINGER, pp. 271–421. New York: John Wiley.
SALOMON, R. G., FOLTING, K., STREIB, W. E. & KOCHI, J. K. (1974). *J. Am. Chem. Soc.* **96**, 1145–1151.
SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determintion. Univ. of Cambridge, England.
SPEE, T., EVERS, J. TH. M. & MACKOR, A. (1982). *Tetrahedron*, **38**, 1311–1319.
SPEK, A. L. (1982). The *EUCLID* package. In *Computational Crystallography*, edited by D. SAYRE p. 528. Oxford: Clarendon Press.
TIMMERMANS, P. J. J. A., MACKOR, A. & SPEK, A. L. (1985). In preparation.
TIMMERMANS, P. J. J. A., DE RUITER, G. M. J., TINNEMANS, A. H. A. & MACKOR, A. (1983). *Tetrahedron Lett.* **24**, 1419–1422.

Acta Cryst. (1985). C**41**, 113–116

Structure of *N,N'*-Di-*tert*-butylethanediimine, $C_{10}H_{20}N_2$, at 98 K and Comparison with the Geometry Calculated by Molecular Mechanics

BY C. J. M. HUIGE AND A. L. SPEK*

Vakgroep Algemene Chemie, afdeling Kristal- en Structuurchemie, Universiteit van Utrecht, Padualaan 8, 3508 TB Utrecht, The Netherlands

AND J. L. DE BOER

Materials Science Centre, Laboratorium voor Anorganische Chemie, Nijenborgh 16, 9747 AG Groningen, The Netherlands

(*Received* 18 *July* 1984; *accepted* 17 *September* 1984)

Abstract. $M_r = 168{\cdot}29$, monoclinic, $P2_1/n$, $a = 9{\cdot}662\,(2)$, $b = 10{\cdot}643\,(2)$, $c = 11{\cdot}472\,(2)$ Å, $\beta = 110{\cdot}15\,(1)°$, $U = 1107{\cdot}5\,(4)$ Å^3, $Z = 4$, $D_x = 1{\cdot}009$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}32$ cm^{-1}, $F(000) = 376$, $T = 98$ K, $R = 0{\cdot}0461$ for 2593 observed reflections. The low-temperature structure contains two independent molecules that are located on $\bar{1}$ symmetry sites. The ethanediimine moiety is in the *trans* conformation. The detailed geometry with its distortion in the *tert*-butyl bond angles is well reproduced by molecular-mechanics calculations.

Introduction. The gas-phase structure of the title compound, which sublimes at room temperature, was studied by Hargittai & Seip (1976) with electron diffraction (ED) techniques. At 353 K a mixture of 80% *gauche* ($\varphi = 65°$) and 20% *trans* ($\varphi = 180°$) conformers around the central C—C bond was found, both with an *E* configuration about the imine bonds. In all cases one C—C bond of the *tert*-butyl moiety is eclipsed with the nearest C=N bond.

In solution a torsion angle (φ) of 90–140° was derived from dipole-moment measurements on this compound (Exner & Kliegman, 1971) and experimental difference of ^{1}H NMR spectra with and without

---

* Author to whom correspondence should be addressed.

0108-2701/85/010113-04$01.50

protonation could be explained by assuming easy access to the single protonated *E-syn-E* planar five-membered ring in related diimines (*e.g.* cyclohexyl substituted for *tert*-butyl, Kliegman & Barnes, 1970). The X-ray structure of the cyclohexyl derivative was recently determined and resulted in a planar *E-trans-E* conformation of the C—N=C—C=N—C system (Keijsper *et al.*, 1983).

As a ligand the conformation of this compound has been determined several times by X-ray work. For the case where both N atoms bind to one metal (σ,σ coordination, *e.g.* Graham, Akrigg & Sheldrick, 1983) an *E-syn-E* conformation was found with both *tert*-butyl groups rotated from the free-ligand conformation (ED structure) by a torsion angle of 60° around the C—N bond, giving a methyl group eclipsed with the N—metal bond.

We have recently developed a potential-energy function for consistent force-field calculations (molecular mechanics) on imines (Huige, 1984). Our aim is to use this function for *a priori* conformational calculations of poly(iminomethylenes) and in view of the importance of torsional behaviour around the central C—C bond of the N=C—C=N moiety in these polymers we are interested in possible non-planar conformations of the title compound in the solid. Earlier work on a somewhat modified N=C—C=N moiety in 2,2'-bipyrimidine gave a non-planar conformation in the gas phase but a planar conformation in the solid due to packing forces (Fernholt, Rømming & Samdal, 1981).

Strain-energy minimization (molecular mechanics) of the free molecule of this compound gives a low *gauche* ($\varphi = 54{\cdot}4°$)/*trans* barrier and the calculated conformer populations at 353 K (ED experimental temperature) are $g{:}t = 0{\cdot}296{:}0{\cdot}704$. The *trans* form, compared to the *gauche* form, is favoured in strain energy by an amount of 3·8 kJ mol^{-1}. Finer structural details, not given by the constrained ED solution but which can be obtained by X-ray work, are now to be compared with our molecular-mechanics results to evaluate the reliability of our potential-energy function, which was fitted to gas-phase structures of small imines (including vibrational frequencies) and to the gas-phase structures of this compound. This study was undertaken since the corresponding room-temperature structure was found to be disordered. The latter will be presented elsewhere (Huige, 1984) along with a comparison with the low-temperature structure.

Experimental. Enraf–Nonius CAD-4F diffractometer, Mo $K\alpha$ (graphite monochromator). Block-shaped (approx. 0·3 × 0·3 × 0·3 mm) transparent colourless crystal, grown by sublimation in a refrigerator at 278 K and mounted on top of a glass fiber ($\theta \leq 32°$, $\omega/2\theta$ scan). Nitrogen cooling with on-line controlled temperature (de Boer & Duisenberg, 1984). 4289 reflections (h: $-14\rightarrow13$, k: $0\rightarrow15$, l: $0\rightarrow17$) collected and corrected for Lorentz–polarization; no correction for absorption. Three reference reflections (310, $\sigma = 1{\cdot}7\%$; $0\bar{3}2$, $\sigma = 1\%$; 022, $\sigma = 1\%$) showed no significant decay during the 36 h of X-ray exposure time (measured every h). Cell parameters determined from setting angles of 18 reflections ($18 < \theta < 19{\cdot}5°$). 3832 unique reflections of which 2593 observed with $I > 2{\cdot}5\sigma(I)$. Structure solved by direct methods and refined by full-matrix least-squares techniques on F; all non-H atoms with anisotropic thermal parameters and H atoms with isotropic thermal parameters, and all positional parameters refined; H-atom positions from a difference Fourier map. Empirical extinction correction $F(\text{corr}) = F(1 - 0{\cdot}0001gF^2/\sin\theta)$, $g = 0{\cdot}0031$ (6), applied. Final $R = 0{\cdot}0461$, $wR = 0{\cdot}0441$, $w^{-1} = [\sigma^2(F) + 0{\cdot}000075F^2]/1{\cdot}879$; $S = 0{\cdot}34$; $\Delta/\sigma < 0{\cdot}7$; 2593 reflections; 190 parameters. Min. and max. residual densities $-0{\cdot}19$ and $0{\cdot}42$ e Å^{-3} (near bond centres).

Scattering factors from Cromer & Mann (1968). All calculations carried out on either the Cyber-175 of the University of Utrecht with programs of the *MULTAN*80 (Main *et al.*, 1980) and *EUCLID* (Spek, 1982) packages or on the in-house Eclipse-S/230 mini-computer with a locally adapted version of the *SHELX*76 package (Sheldrick, 1976). Molecular-mechanics calculations with locally adapted version of the *CFF* program (Niketic & Rasmussen, 1977; Rasmussen, 1983).

Discussion. The final parameters are given in Table 1.* The unit cell of the low-temperature structure of the title compound contains four molecules that are located at sites with $\bar{1}$ symmetry. Thus the asymmetric unit contains two independent half-molecules as shown in Fig. 1 (along with the adopted numbering scheme). The packing of the molecules is dominated by the *tert*-butyl groups that exhibit approximate translation symmetry in the **c** direction with the N=C—C=N planes in two different orientations as illustrated in Fig. 2. The corresponding room-temperature structure turns out to be similar, but, in view of a phase transition at 253 K to a cell with translation period $\sim\frac{1}{2}$ **c**, disordered with the occurrence of both N=C—C=N plane orientations at the same molecular site (Huige, 1984).

Relevant data on the geometry are given in Table 2, together with the molecular-mechanics results for the *trans* conformation. There are no significant differences in the experimental bond distances and bond angles between both molecules. However, there are small but

---

* Lists of structure factors, anisotropic thermal parameters and bond distances and angles involving H atoms together with molecular-mechanics results for positional and geometrical parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39731 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final coordinates and isotropic thermal parameters*

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

	x	y	z	U_{eq}(Å^2)
N(2)	0·0892 (1)	0·06323 (9)	0·40364 (9)	0·0177 (2)
N(8)	0·1194 (1)	0·11869 (9)	0·98710 (9)	0·0179 (2)
C(1)	0·0683 (1)	0·0321 (1)	0·5028 (1)	0·0171 (2)
C(3)	0·2275 (1)	0·1261 (1)	0·4086 (1)	0·0164 (2)
C(4)	0·3028 (1)	0·0362 (1)	0·3456 (1)	0·0236 (3)
C(5)	0·3326 (1)	0·1590 (1)	0·5389 (1)	0·0200 (3)
C(6)	0·1824 (1)	0·2457 (1)	0·3312 (1)	0·0249 (3)
C(7)	0·0584 (1)	0·0117 (1)	0·9739 (1)	0·0175 (2)
C(9)	0·2392 (1)	0·1435 (1)	0·9376 (1)	0·0166 (2)
C(10)	0·3705 (1)	0·1859 (1)	1·0491 (1)	0·0220 (3)
C(11)	0·2831 (1)	0·0324 (1)	0·8741 (1)	0·0219 (3)
C(12)	0·1861 (1)	0·2522 (1)	0·8460 (1)	0·0261 (3)
H(11)	0·1352 (8)	0·0484 (7)	0·5842 (7)	0·0221 (9)
H(41)	0·3346 (8)	−0·0417 (8)	0·3938 (7)	0·0263 (9)
H(42)	0·3914 (8)	0·0745 (7)	0·3403 (7)	0·0231 (9)
H(43)	0·2362 (8)	0·0149 (7)	0·2595 (8)	0·0269 (9)
H(51)	0·2861 (8)	0·2134 (7)	0·5837 (7)	0·0229 (9)
H(52)	0·3663 (8)	0·0820 (7)	0·5899 (7)	0·0220 (9)
H(53)	0·4216 (8)	0·2006 (7)	0·5331 (7)	0·0244 (9)
H(61)	0·2691 (8)	0·2913 (8)	0·3260 (7)	0·0257 (9)
H(62)	0·1288 (8)	0·3048 (8)	0·3691 (7)	0·0253 (9)
H(63)	0·1167 (8)	0·2261 (7)	0·2453 (7)	0·0259 (9)
H(71)	0·0839 (8)	−0·0593 (7)	0·9333 (7)	0·0233 (9)
H(101)	0·4061 (8)	0·1162 (7)	1·1096 (7)	0·0241 (9)
H(102)	0·4528 (8)	0·2120 (7)	1·0222 (7)	0·0217 (9)
H(103)	0·3452 (8)	0·2570 (7)	1·0902 (7)	0·0241 (9)
H(111)	0·2009 (8)	0·0012 (7)	0·8066 (8)	0·0235 (9)
H(112)	0·3230 (8)	−0·0398 (8)	0·9327 (7)	0·0255 (9)
H(113)	0·3579 (8)	0·0578 (7)	0·8431 (7)	0·0246 (9)
H(121)	0·1545 (8)	0·3239 (8)	0·8848 (7)	0·0264 (9)
H(122)	0·2657 (8)	0·2797 (7)	0·8170 (7)	0·0255 (9)
H(123)	0·1018 (8)	0·2266 (7)	0·7734 (7)	0·0260 (9)

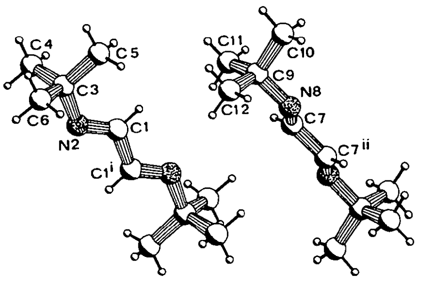

Fig. 1. Drawing of the two independent molecules with site symmetry $\bar{1}$, as viewed down the b axis.

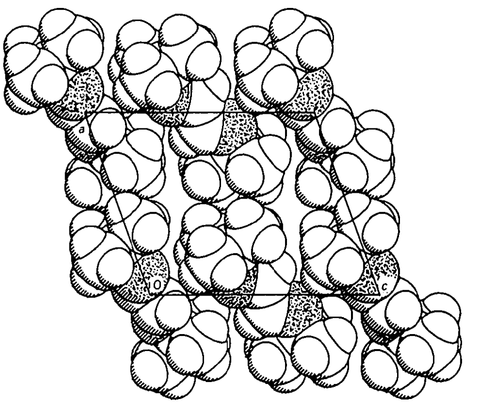

Fig. 2. Space-filling view down the b axis of the packing of the molecules in the $b \approx 0$ level. This layer is superimposed by a similar one at $b \approx \frac{1}{2}$ *via* the screw axis passing through $x = z = \frac{1}{4}$. N atoms are indicated by dotted spheres.

Table 2. *Selected data on the molecular geometry and comparison with molecular-mechanics results(MM)*

(*a*) Bond distances (Å)				MM
N(2)–C(1)	1·267 (2)	N(8)–C(7)	1·267 (1)	1·278
N(2)–C(3)	1·478 (1)	N(8)–C(9)	1·478 (1)	1·463
C(1)–C(1^{i})	1·467 (2)	C(7)–C(7^{ii})	1·470 (2)	1·498
C(3)–C(5)	1·530 (2)	C(9)–C(11)	1·524 (2)	1·540
C(3)–C(4)	1·527 (2)	C(9)–C(10)	1·528 (2)	1·530
C(3)–C(6)	1·527 (2)	C(9)–C(12)	1·528 (2)	1·530
(*b*) Bond angles (°)				MM
C(1)–N(2)–C(3)	120·4 (1)	C(7)–N(8)–C(9)	120·5 (1)	121·7
N(2)–C(1)–C(1^{i})	120·1 (1)	N(8)–C(7)–C(7^{ii})	119·6 (1)	120·3
N(2)–C(3)–C(5)	115·4 (1)	N(8)–C(9)–C(11)	115·4 (1)	118·8
N(2)–C(3)–C(4)	105·7 (1)	N(8)–C(9)–C(10)	105·4 (1)	105·9
N(2)–C(3)–C(6)	106·3 (1)	N(8)–C(9)–C(12)	106·1 (1)	105·9
C(4)–C(3)–C(5)	110·0 (1)	C(11)–C(9)–C(12)	110·0 (1)	108·3
C(5)–C(3)–C(6)	109·7 (1)	C(11)–C(9)–C(10)	110·0 (1)	108·3
C(4)–C(3)–C(6)	109·5 (1)	C(10)–C(9)–C(12)	109·7 (1)	109·5
(*c*) Torsion angles (°)				MM
C(1^{i})–C(1)–N(2)–C(3)	−179·0 (1)	C(7^{ii})–C(7)–N(8)–C(9)	178·8 (1)	180·0
C(1)–N(2)–C(3)–C(5)	−5·0 (1)	C(7)–N(8)–C(9)–C(11)	−1·2 (1)	0·0

Symmetry code: (i) $-x, -y, 1-z$; (ii) $-x, -y, 2-z$.

significant differences in some of the torsion angles, probably due to packing.

In both molecules the C=N bonds are approximately coplanar with one of the C—CH_3 bonds. This results in a high steric hindrance in this plane with strong distortion of the C—C—C angles in the *tert*-butyl groups and also with shrinkage of the C(1^{i})—C(1)—H(1) angle [115·2 (5)°] [C(7^{ii})—C(7)—H(71), 115·1 (5)°] from the usual 120°. Thus the tendency of one methyl group to eclipse the C=N bond must be a strong effect. An equal tendency for the C=C bond can be found for example in 1,1-di-*tert*-butyl-2,2-diphenylethylene although here it cannot be completely fulfilled due to very strong steric hindrance (Mugnoli & Simonetta, 1976). The deviations of atoms C(3) and C(5) [C(9) and C(11)] from the central planes through the atoms N(2)-C(1)C(1^{i})N(2^{i}) [N(8)C(7)C(7^{ii})N(8^{ii})] are −0·02 (1) and 0·08 (1) Å [0·03 (2) and 0·08 (2) Å]. As a result of the above-mentioned pseudotranslation and the eclipsed methyl groups both planes make a dihedral angle of 63·3 (2)° with each other. Ideally this angle is 60° and the small difference is in agreement with the difference between the C(1)N(2)C(3)C(5) and C(7)N(8)C(9)-C(11) torsion angles (Table 2).

The central C—C bond length {1·467 (2) [1·470 (2)] Å} compares well with the central bond length in 1,3-butadiene [1·467 (2) Å, Kveseth, Seip & Kohl, 1980] and indicates the presence of normal conjugation. This may be compared with strong conjugation as reflected by the glyoxime central bond [1·453 (1) Å, Jeffrey, Ruble & Pople, 1982] or with conjugation which is hindered by repulsion in the 2,2′-bipyrimidine solid [1·497 (4) Å, Fernholt *et al.*, 1981].

The C=N bond lengths {1·267 (2) [1·267 (1)] Å} are in the normal range of this type of bond and stand somewhat in contrast to the corresponding 1·2849 (9) Å in glyoxime.

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, $a = 8{\cdot}440\ (9)$, $b = 8{\cdot}037\ (5)$, $c = 12{\cdot}81\ (1)$ Å, $\beta = 92{\cdot}87\ (6)°$, $V = 868\ (1)$ Å^3, $Z = 2$, $D_x = 1{\cdot}385\ (5)$, $D_m = 1{\cdot}37\ (4)$ Mg m^{-3}, $\lambda(\text{Mo } K\bar{\alpha}) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}34$ mm^{-1}, $F(000) = 400$, $T = 293$ K. Final $R = 0{\cdot}039$ 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