through an O3′···O5′ hydrogen-bonding scheme parallel to the *b* axis. The second anomaly implies that distinct conformers are paired across the twofold axis. The refined occupancy of 50% also confirms this pairing. The paired chains of conformers must be randomly distributed through the lattice, which is plausible since all other hydrogen-bonding interactions are between non-unique atoms of the two conformers. The nitro groups of one chain are intercalated between the pyrimidine rings (specifically, atoms N1, C2, N3) of the adjacent chain related by *C*-centering. This arrangement supports the planarity of the aglycon moiety. The nitro group is 2·973 (6) and 3·130 (6) Å from the sandwiching pyrimidine rings.

References

Altona, C. & Sundaralingam, M. (1972). *J. Am. Chem. Soc.* **94**, 8205–8212.

Ammon, H. L. & Bhattacharjee, S. K. (1982). *Acta Cryst.* B**38**, 2083–2086.

Ammon, H. L., Bhattacharjee, S. K. & Holden, J. R. (1982). *Acta Cryst.* B**38**, 1851–1854.

Ammon, H. L. & Prasad, S. M. (1985). *Acta Cryst.* C**41**, 921–924.

Berman, H. M., Rousseau, R. J., Mancuso, R. W., Kreishman, G. P. & Robins, R. K. (1973). *Tetrahedron Lett.* **33**, 3099–3101.

Bhattacharjee, S. K. & Ammon, H. L. (1981). *Acta Cryst.* B**37**, 2082–2085.

Cady, H. H. & Larson, A. C. (1965). *Acta Cryst.* **18**, 485–496.

Cambridge Structural Database (1987). Univ. Chemical Laboratory, Lensfield Road, Cambridge, England.

Cordes, A. W. (1983). Personal communication.

Frenz, B. A. (1985). *Enraf–Nonius SDP-Plus Structure Determination Package.* Version 3.0. Enraf–Nonius, Delft, The Netherlands.

Holden, J. R. (1967). *Acta Cryst.* **22**, 545–550.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee. USA.

Kubo, I., Kim, M., Wood, W. F. & Naoki, H. (1986). *Tetrahedron Lett.* **27**, 4277–4280.

Main, P., Fiske, H. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1982). *MULTAN*82. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Moss, R. J., Petrie, C. R., Meyer, R. B. Jr, Nord, L. D., Willis, R. C., Smith, R. A., Larson, S. B., Kini, G. D. & Robins, R. K. (1988). *J. Med. Chem.* In the press.

Narayanan, P. & Berman, H. M. (1975). *Carbohydr. Res.* **44**, 169–180.

Sheldrick, G. M. (1976). *SHELX*76. *Program for crystal structure determination.* Univ. of Cambridge, England.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1988). C**44**, 1080–1083

Reaction of 3-Azidopropanol with Tris(dimethylamido)phosphorus and Structure of the Phosphazide Reaction Product

By Connie G. Chidester, Jacob Szmuszkovicz, David J. Duchamp and Lloyd G. Laurian

Research Laboratories, The Upjohn Company, Kalamazoo, MI 49001, *USA*

and Jeremiah P. Freeman

Department of Chemistry, Notre Dame University, Notre Dame, IN 46556, *USA*

(*Received* 26 *September* 1987; *accepted* 23 *February* 1988)

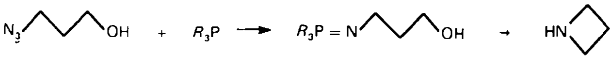
Abstract. 3-{3-[Tris(dimethylamino)phosphoranylidene]-1-triazenyl}-1-propanol, $C_9H_{25}N_6OP$, $M_r = 264{\cdot}31$, monoclinic, $P2_1/c$, $a = 8{\cdot}112\ (1)$, $b = 17{\cdot}497\ (1)$, $c = 10{\cdot}554\ (1)$ Å, $\beta = 104{\cdot}87\ (1)^\circ$, $V = 1447{\cdot}8\ (2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}21$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}5418$ Å, $\mu = 1{\cdot}6$ cm^{-1}, $F(000) = 576$, $T = 123$ K, $R = 0{\cdot}046$ for 2511 unique reflections. One of the dimethylamino N atoms deviates more from planarity than the other two and this P—N bond is significantly longer than the other P—N bonds. The azide bonds are not delocalized. This is apparently the first crystal structure of a phosphazide. The dimethylamino substituents on the P atom enhanced the stability of this phosphazide intermediate in a Staudinger reaction with 3-azidopropanol. In analogous reactions with phenyl or *n*-butyl substituents on the P atom only later phosphazo intermediates could be isolated.

Introduction. We have been interested in the Staudinger reaction (Gololobov, Zhmurova & Kasukhin, 1981) of 3-azidopropanol (1) with phosphines, and were successful in applying this reaction to the syntheses of azetidine (3) when triphenyl or tri-*n*-butylphosphine was used (Szmuszkovicz, Kane, Laurian, Chidester & Scahill, 1981). In the course of the above, we isolated the phosphazo intermediates (2*a*) and (2*b*) and reported

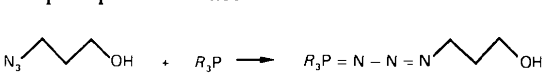
0108-2701/88/061080-04$03.00

© 1988 International Union of Crystallography

the crystal structure determination of (2*a*). A phosphazide intermediate, however, could not be isolated although the reaction was performed under mild conditions.


(1) (2) (2*a*) $R = C_6H_5$ (3)
(2*b*) $R = n-C_4H_9$

We then became interested in the mechanism of the Staudinger reaction. In the hope that an earlier intermediate would be isolated, we reacted (1) with tris(dimethylamido)phosphorus (4) and obtained the phosphazide (5*a*). We report here the crystal and molecular structure of (5*a*), which appears to be the first X-ray determination of a representative compound of the phosphazide class.


(1) (4) $R = (CH_3)_2N$ (5*a*) $R = (CH_3)_2N$
(5*b*) $R = C_6H_5$

As we expected, in the case of (5*a*) the stability of the phosphazide molecule has been enhanced [as compared to the hypothetical phosphazide intermediate from (1) and triphenyl- or tri-*n*-butylphosphine] by electronic factors (conjugative delocalization of the charge on the P atom) and steric factors; however, (5*a*) is itself unstable at temperatures above about 263 K.

Experimental. Clear chunky prism 0·21 × 0·19 × 0·28 mm, crystallized at room temperature from diethyl ether and stored at 263 K; Nicolet $P2_1$ diffractometer controlled by Harris computer; graphite monochromator, Cu $K\alpha$; $2\theta_{max} = 138°$; all 2511 unique reflections measured, 2164 had intensities $>2\sigma$; $2°\ min^{-1}$ $\theta/2\theta$ step scans, scan widths $\geq 3·4°$ (Duchamp, 1977); 10 reflections periodically monitored showed no trend towards deterioration; $\sigma^2(I)$ was approximated by $\sigma^2(I)$ from counting statistics + $(0·037I)^2$, where the coefficient of I was calculated from the variations in intensities of the monitored reflections; cell parameters by least-squares fit of $K\alpha_1$ 2θ values, $\lambda(\text{Cu } K\alpha_1) = 1·5402$ Å for 22 high-2θ reflections (Duchamp, 1977); Lp correction appropriate for a monochromator with 50% perfect character; no absorption correction.

The structure was solved by direct methods, using *DIREC* (Duchamp, 1984); H atoms were found in difference maps. Least-squares refinement included all coordinates and anisotropic thermal parameters for non-H atoms. Isotropic thermal parameters for H atoms were 0·5 Å^2 higher than attached atoms. The function minimized in the refinement was $\sum w(F_o^2 - F_c^2)^2$, where weights w were $1/\sigma^2(F_o^2)$. Atomic form factors were from Doyle & Turner (1968), and, for H, from Stewart, Davidson & Simpson (1965). All 2511 reflections were used in the refinement. In the final cycle, all shifts were $<0·25\sigma$, $R = 0·046$, $wR = 0·094$, $S = 1·73$, final difference Fourier peaks were $<0·3$ e Å^{-3}. The *CRYM* system of computer programs was used (Duchamp, 1984).

Discussion. Final atomic parameters are listed in Table 1.* Fig. 1 shows conformation and numbering. Bond distances and angles are given in Table 2. The N atoms in the dimethylamino groups, although not quite planar, certainly do not have tetrahedral geometry; bond angles at these three N atoms sum to 357·7 (2), 357·2 (2) and 353·6 (2)°. It is interesting that the N atom which is less planar than the others, N(10), also has a longer bond to the P atom, 1·651 (1) Å, compared to 1·638 (1) and 1·639 (1) Å. Rettig & Trotter (1973), reporting the structure of 2,2,4,4,6,6-hexakis(dimethylamino)cyclotriphosphazene, observed that the two dimethylamino groups bonded to each of the three P atoms in the ring were apparently not equivalent. In all three cases, one of each pair of N atoms was more planar than the other; the mean sums of angles around the N atoms were 357·3 (2)° for the more planar groups and 349·3 (2)° for the less planar groups. However, in a study of a cyclodiphosphazene with diisopropylamino substituents (Baceiredo, Bertrand, Majoral, Sicard, Jaud & Galy, 1984), all the P—N bonds, both exo- and endocyclic, were equal [bond lengths were 1·644 (9)–1·651 (8) Å], and the N atoms were planar, within experimental error, indicating extensive delocalization.

In the structure reported here, the electron density in the N=N and N—C bonds is not delocalized; bond lengths are very similar to the N=N and N—C bond lengths in azomethane (Chang, Porter & Bauer, 1970). The P=N bond is 1·615 (1) Å in this structure, longer than the P=N bond in (2*a*), which is 1·570 (3) Å. The adjacent N—N bond is 1·375 (2) Å, somewhat shorter than a normal N—N single bond, which should be 1·451 Å (Sutton, 1965). This apparent delocalization does not occur in (2*a*), where the N—C bond adjacent to the P=N bond is 1·482 (5) Å, which is the expected N—C single-bond length (Marsh, Bierstedt & Eichhorn, 1962). There is an O—H···N hydrogen bond between O(7) and N(1) in the molecule related by $2-x$, $-y$, $1-z$. The O···N distance is 2·845 (2) Å, and the angle at the H atom is 173 (1)°. There are no other intermolecular distances less than 3·6 Å.

---

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, bond lengths to H atoms and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44802 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

In the reaction scheme postulated in the *Introduction,* the intermediate in going from the phosphazide (5) to the phosphazo compound (2) is probably the elusive compound (6) (Gololobov *et al.*, 1981; Goldwhite, Gysegem, Schow & Swyke, 1975; Leffler & Temple, 1967); (6) has never been isolated, as it apparently rearranges very quickly to the phosphazo compound (2).

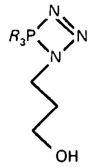

(6) (6*a*) $R = (CH_3)_2N$
(6*b*) $R = C_6H_5$

Table 1. *Fractional coordinates* ($\times 10^4$) *and* B_{eq} (Å^2) *values*

$B_{eq} = \frac{4}{3}(a^2B_{11} + b^2B_{22} + c^2B_{33} + ab\cos\gamma B_{12} + ac\cos\beta B_{13} + bc\cos\alpha B_{23})$.

	x	y	z	B_{eq}
P	7553 (1)	1435 (1)	379 (1)	1·11 (1)
N(1)	8255 (2)	1179 (1)	1893 (1)	1·44 (5)
N(2)	9999 (2)	1244 (1)	2315 (1)	1·40 (5)
N(3)	10580 (2)	947 (1)	3424 (1)	1·65 (6)
C(4)	12439 (2)	1051 (1)	3881 (2)	1·69 (6)
C(5)	13021 (2)	880 (1)	5346 (2)	1·79 (7)
C(6)	12839 (2)	49 (1)	5658 (2)	2·00 (7)
O(7)	13566 (2)	−76 (1)	7021 (1)	2·82 (6)
N(8)	5534 (2)	1611 (1)	252 (1)	1·35 (5)
C(8*A*)	4326 (2)	1640 (1)	−1038 (2)	1·90 (7)
C(8*B*)	4910 (3)	1958 (1)	1302 (2)	2·02 (7)
N(9)	7788 (2)	752 (1)	−624 (1)	1·40 (5)
C(9*A*)	7677 (3)	852 (1)	−2017 (2)	2·15 (7)
C(9*B*)	7568 (3)	−45 (1)	−272 (2)	2·04 (7)
N(10)	8399 (2)	2176 (1)	−190 (1)	1·48 (5)
C(10*A*)	10135 (2)	2134 (1)	−357 (2)	2·33 (8)
C(10*B*)	7903 (3)	2952 (1)	57 (2)	2·09 (7)

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

P—N(1)	1·615 (1)	C(5)—C(6)	1·506 (3)
P—N(8)	1·638 (1)	C(6)—O(7)	1·424 (2)
P—N(9)	1·639 (1)	N(8)—C(8*A*)	1·460 (2)
P—N(10)	1·651 (1)	N(8)—C(8*B*)	1·463 (2)
N(1)—N(2)	1·375 (2)	N(9)—C(9*A*)	1·460 (2)
N(2)—N(3)	1·256 (2)	N(9)—C(9*B*)	1·467 (2)
N(3)—C(4)	1·472 (2)	N(10)—C(10*A*)	1·465 (2)
C(4)—C(5)	1·526 (3)	N(10)—C(10*B*)	1·458 (2)

N(1)—P—N(8)	103·0 (1)	C(5)—C(6)—O(7)	109·3 (2)
N(1)—P—N(9)	111·6 (1)	P—N(8)—C(8*A*)	120·1 (1)
N(1)—P—N(10)	120·2 (1)	P—N(8)—C(8*B*)	123·3 (1)
N(8)—P—N(9)	111·3 (1)	C(8*A*)—N(8)—C(8*B*)	114·3 (1)
N(8)—P—N(10)	108·8 (1)	P—N(9)—C(9*A*)	125·2 (1)
N(9)—P—N(10)	102·1 (1)	P—N(9)—C(9*B*)	119·2 (1)
P—N(1)—N(2)	111·7 (1)	C(9*A*)—N(9)—C(9*B*)	112·8 (2)
N(1)—N(2)—N(3)	112·1 (1)	P—N(10)—C(10*A*)	120·4 (1)
N(2)—N(3)—C(4)	111·2 (1)	P—N(10)—C(10*B*)	120·5 (1)
N(3)—C(4)—C(5)	109·4 (1)	C(10*A*)—N(10)—C(10*B*)	112·7 (1)
C(4)—C(5)—C(6)	112·9 (2)		

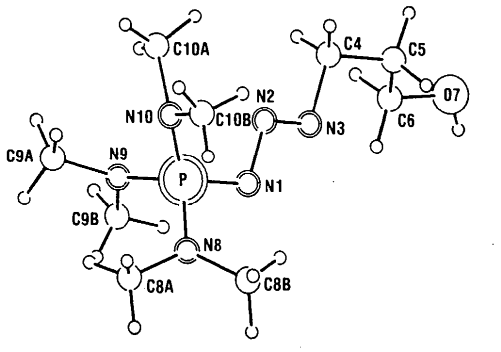


Fig. 1. Numbering and conformation of (5*a*).

Evidently, the compound reported here, (5*a*), which has dimethylamino substituents on the P atom, is more stable than the analogous postulated triphenylazide intermediate. One possible explanation for the difference in stability is that the electronic state of the P atom, when it is already bonded to four N atoms, is such that it is less susceptible to attack by a fifth N atom. Another possibility, which we were better equipped to investigate, is that the less bulky and more distant phenyl substituents leave the P atom more open to attack than when the substituents are dimethylamino. The molecular-mechanics program *CONFOS* (Duchamp, Pschigoda & Chidester, 1987) was used to calculate the changes in energy as both (5*a*), the dimethylaminophosphazide reported in this paper, and (5*b*), the postulated analogous triphenylazide, were made to approach the conformation expected for the pentavalent intermediate (6).

The hypothetical compound (6) was modeled, for R = dimethylamino and for R = phenyl, using three pentavalent phosphorus compounds from the literature (Day, Schmidpeter & Holmes, 1983; Weferling, Schmutzler & Sheldrick, 1982; Haller, Scheffler, Stegmann & Winter, 1981). These and other pentavalent phosphorus molecules have approximately bipyramidal conformations around the P atom. Since the ring N—P—N angle must be less than 90°, one of the ring N atoms must be axial and the other equatorial with respect to the P atom. One of these N atoms has a $(CH_2)_3OH$ substituent, and because the three other substituents on the P atom are all the same, there are only two conformations to consider, either the substituent is on the axial N atom or it is on the equatorial N atom. Molecular-mechanics calculations using *CONFOS* indicated that for each R = phenyl and R = dimethylamino, the conformation with the substituent on the equatorial N atom was lower in energy by about 18·8 kJ. The two models with ring substituents on the equatorial N atoms were energy minimized and used as target conformations for a series of calculations on (5*a*) and (5*b*) using extra potentials (Duchamp *et al.*, 1987) to force their conformations to approach the target. To verify that *CONFOS* was parametrized correctly for these structures, calculations on (5*a*) and on a PN_5 structure from the literature (Day *et al.*, 1983) were performed 'in the crystal', *i.e.* with surrounding symmetry-related atoms included, and these did indeed reproduce the crystal structures with only small discrepancies. Several starting conformations for (5*a*) and (5*b*) were explored and from each a six-step approach to the target was forced. Considering only the lowest-energy paths, we found that the increase in energy of (5*b*) as it approached the (6*b*) target conformation was 6·3 to 8·4 kJ less than the energy increase of (5*a*) as it approached the (6*a*) conformation. This is a quantitation of the idea that the more bulky dimethylamino groups, which are also closer to the P atom, make it more difficult for the azide N atom to approach the P atom than when the substituents are phenyl groups.

References

BACEIREDO, A., BERTRAND, G., MAJORAL, J.-P., SICARD, G., JAUD, J. & GALY, J. (1984). *J. Am. Chem. Soc.* **106**, 6088–6089.

CHANG, C. H., PORTER, R. F. & BAUER, S. H. (1970). *J. Am. Chem. Soc.* **92**, 5313–5318.

DAY, R. O., SCHMIDPETER, A. & HOLMES, R. R. (1983). *Inorg. Chem.* **22**, 3696–3699.

DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* A**24**, 390–397.

DUCHAMP, D. J. (1977). *Am. Chem. Soc. Symp. Ser.* No. 46, pp. 98–121.

DUCHAMP, D. J. (1984). *CRYM. A System of Crystallographic Programs* (including *DIREC, a Direct Methods Program for Solving Crystal Structures*). The Upjohn Company, Kalamazoo, MI, USA.

DUCHAMP, D. J., PSCHIGODA, L. M. & CHIDESTER, C. G. (1987). *Proceedings of the International Symposium on Molecular Structure*, Beijing, China, September 1986. In the press.

GOLDWHITE, H., GYSEGEM, P., SCHOW, S. & SWYKE, C. (1975). *J. Chem. Soc. Dalton Trans.* pp. 16–18.

GOLOLOBOV, Y. G., ZHMUROVA, I. N. & KASUKHIN, L. F. (1981). *Tetrahedron*, **37**, 437–472.

HALLER, R., SCHEFFLER, K., STEGMANN, H. B. & WINTER, W. (1981). *Chem. Ber.* **114**, 447–455.

LEFFLER, J. E. & TEMPLE, R. D. (1967). *J. Am. Chem. Soc.* **89**, 5235–5246.

MARSH, R. E., BIERSTEDT, R. & EICHHORN, E. L. (1962). *Acta Cryst.* **15**, 310–316.

RETTIG, S. J. & TROTTER, J. (1973). *Can. J. Chem.* **51**, 1295–1302.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

SUTTON, L. E. (1965). *Tables of Interatomic Distances and Configuration in Molecules and Ions. Supplement.* Spec. Publ. No. 18. London: The Chemical Society.

SZMUSZKOVICZ, J., KANE, M. P., LAURIAN, L. G., CHIDESTER, C. G. & SCAHILL, T. A. (1981). *J. Org. Chem.* **46**, 3562–3564.

WEFERLING, N., SCHMUTZLER, R. & SHELDRICK, W. S. (1982). *Justus Liebigs Ann. Chem.* pp. 167–181.

Acta Cryst. (1988). C**44**, 1083–1086

Structure of 4-Hydroxy-1,2-benzisothiazol-3(2*H*)-one 1,1-Dioxide Sodium Salt (UH-AF 50 NA) at 123 K based on Neutron Diffraction Data

BY R. RUDERT, J. BUSCHMANN AND P. LUGER

Institut für Kristallographie der Freien Universität Berlin, Takustrasse 6, *D*-1000 *Berlin* 33, *Federal Republic of Germany*

D. GREGSON

Institut für Kristallographie der Universität Frankfurt, Senckenberganlage 30, *D*-6000 *Frankfurt* 1, *Federal Republic of Germany*

AND G. TRUMMLITZ

Dr K. Thomae GmbH, Birkendorfer Strasse 65, *D*-7950 *Biberach, Federal Republic of Germany*

(*Received* 11 *May* 1987; *accepted* 24 *December* 1987)

Abstract. $Na^+.C_7H_4NO_4S^-.H_2O$, $M_r = 239{\cdot}2$, orthorhombic, *Pnam*, $a = 10{\cdot}842\,(6)$, $b = 12{\cdot}042\,(6)$, $c = 6{\cdot}910\,(1)$ Å, $V = 902{\cdot}2$ Å^3, $Z = 4$, $D_N = 1{\cdot}760$ g cm^{-3}, $\lambda_N = 1{\cdot}1756$ Å, $\mu = 1{\cdot}194$ cm^{-1}, $F(000) = 488$, $T = 123$ K, final $R(F^2) = 0{\cdot}079$, $wR(F^2) = 0{\cdot}110$ for 937 independent observed reflections. The molecule lies on the mirror plane except for the SO_2 O atoms and the water H atoms. The Na^+ cation has sixfold coordination with one N and five O atoms in a distorted octahedron.

Introduction. As part of a program to investigate charge-density distributions of saccharin derivatives, a neutron structure analysis of the title compound, UH-AF 50 NA, was performed to provide accurate atomic parameters for a three-dimensional difference Fourier synthesis of an *X*—*N* deformation electron density distribution that could not be obtained by X-ray diffraction on account of low scattering power at high angles. UH-AF 50 NA is a new non-nutritive sweetener and will be compared with other saccharin derivatives

0108-2701/88/061083-04$03.00

© 1988 International Union of Crystallography