Acta Cryst. (1990). C**46**, 883–886

Structure of 2-Hydroxy-(5-{[4-(2-pyridinylamino)sulfonyl]phenyl}azo)benzoic Acid–*N*,*N*-Dimethylformamide–H_2O (1/0·5/*n*)($n \simeq 2{\cdot}25$)

By P. van der Sluis* and A. L. Spek†

Laboratorium voor Kristal- en Structuurchemie, Rijksuniversiteit Utrecht, Transitorium 3, *Padualaan* 8,
3584 *CH Utrecht, The Netherlands*

(*Received* 17 *July* 1989; *accepted* 30 *August* 1989)

Abstract. $C_{18}H_{14}N_4O_5S.0{\cdot}5C_3H_7NO.nH_2O$ ($n \simeq 2{\cdot}25$), $M_r = 475{\cdot}49$, triclinic, $P\bar{1}$, $a = 7{\cdot}204\,(1)$, $b = 11{\cdot}286\,(1)$, $c = 28{\cdot}203\,(1)$ Å, $\alpha = 87{\cdot}77\,(1)$, $\beta = 87{\cdot}91\,(1)$, $\gamma = 82{\cdot}81\,(1)°$, $V = 2272{\cdot}1\,(4)$ Å^3, $Z = 4$, $D_x = 1{\cdot}39$, $D_m = 1{\cdot}36\,(2)$ Mg m^{-3}, $\lambda(\text{Cu } K\alpha) = 1{\cdot}54184$ Å, $\mu = 1{\cdot}69$ mm^{-1}, $F(000) = 994$, $T = 294$ K, $R = 0{\cdot}045$ for 3122 unique observed diffractometer data [$I \geq 2{\cdot}5\sigma(I)$]. The two crystallographically independent 2-hydroxy-(5-{[4-(2-pyridinylamino)sulfonyl]phenyl}azo)benzoic acid (salazopyrine) molecules are both present in the imide tautomeric form. Their conformational flexibility, as measured by the differing torsion angles about the S—C and S—N bonds, indicates that the crystal lattice plays a rôle in determining the molecular conformation. The two salazopyrine molecules and the *N*,*N*-dimethylformamide (DMF) solvate molecule are joined *via* three types of hydrogen-bond schemes. The water molecules are found in channels running in the **a** direction.

Introduction. Salazopyrine (*The Merck Index*, 1983) is an antibacterial drug and is used to treat illnesses such as colitis ulcerosa and Morbus Crohn. It is split in the large intestine under the influence of bacterial enzymes into sulfapyridine and 5-aminosalicylic acid. The latter compound has been shown to be the active component and is now in use as an alternative drug with the same indications but lacking the side effects that are caused by the sulfapyridine component.

The present study was undertaken to complement the available information on the drug salazopyrine with a crystal structure. No structural investigation has been published previously for this compound, probably due to the difficulty in obtaining suitable crystals. We obtained crystals of improved size and quality by the technique of co-crystallization with a suitable solvent (van der Sluis & Kroon, 1989).

Experimental. The title compound was extracted from tablets (Pharmacia) of the drug salazopyrine using boiling ethanol and was recrystallized by sitting drop vapour diffusion (McPherson, 1976) using DMF as solvent and water as precipitant. Data were collected on a CAD-4F diffractometer for a transparent, orange crystal ($0{\cdot}08 \times 0{\cdot}1 \times 0{\cdot}5$ mm), mounted on a glass fiber. The density was obtained by flotation in aqueous caesium chloride. The cell parameters were calculated by least squares from the setting angles of 17 reflections with $13{\cdot}4 < \theta < 22{\cdot}2°$. 5140 reflections were scanned [h −7:0, k −11:11, l −27:27; $1{\cdot}57 \leq \theta \leq 50°$; $\omega/2\theta$-scan mode; $\Delta\omega = (0{\cdot}50 + 0{\cdot}15\tan\theta)°$; Ni-filtered Cu $K\alpha$ radiation]. Two reference reflections ($0\bar{3}6$, $\bar{2}0\bar{4}$) showed fluctuations of 3%, and a small decay of less than 1% during the 81 hours of X-ray exposure time. The data were corrected for Lp but not for absorption, resulting in the unique set of 3122 reflections [$I > 2{\cdot}5\sigma(I)$] used in the structure determination. $\sigma^2(I) = \sigma^2_{\text{cs}}(I) + (pI)^2$ (McCandlish, Stout & Andrews, 1975) with $p = 0{\cdot}02$. All non-H atoms of the two salazopyrine molecules were found by direct methods with *SHELXS86* (Sheldrick, 1986). The non-H atoms of one DMF molecule were located from a difference Fourier synthesis. The structure was refined on F by full-matrix least-squares procedures using anisotropic thermal parameters for all non-H atoms with *SHELX76* (Sheldrick, 1976). H atoms attached to N and O, involved in hydrogen bonding, could be identified in a difference Fourier map. However, in view of the unfavorable data to parameter ratio only those attached to O were refined (with a bond distance restraint). All other H atoms were introduced at calculated positions (N—H, C—H = 0·98 Å) and refined in the riding mode on their carrier atoms with an isotropic thermal parameter common to all H atoms. Convergence was reached at $R = 0{\cdot}096$ ($wR = 0{\cdot}184$, $w = 1{\cdot}0$). A subsequent difference Fourier map showed infinite channels with nearly continuous residual density along x, centred at $y = 0{\cdot}85$, and $z = 0{\cdot}25$ (Fig. 1). No discrete model could be fitted in this density. The *BYPASS* procedure (van der Sluis & Spek, 1990) was used to take into account the electron density in the channel in the refinement.

At this stage the distance restraint on the O—H bonds could be removed. Final convergence was

---

* Present address: Philips Research Laboratories, PO Box 80.021, 5600 JA Eindhoven, The Netherlands.

† Author to whom correspondence should be addressed.

0108-2701/90/050883-04$03.00

© 1990 International Union of Crystallography

reached at $R = 0{\cdot}045$ [$wR = 0{\cdot}036$, $w = 1{\cdot}8974/\sigma^2(F)$; $S = 1{\cdot}05$; $(\Delta/\sigma)_{\max} = 0{\cdot}67$; number of refined parameters = 571]. No residual density outside the range $-0{\cdot}23$ and $0{\cdot}17\,\mathrm{e\,Å^{-3}}$. Scattering factors from Cromer & Mann (1968), anomalous-dispersion corrections from Cromer & Liberman (1970). The final atomic coordinates and equivalent isotropic temperature factors are listed in Table 1.* The program package *EUCLID* (Spek, 1982) was used for geometrical calculations and illustrations. All calculations were carried out on a MicroVAX-II.

Table 1. *Final coordinates and equivalent isotropic thermal parameters and their e.s.d.'s in parentheses*

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

	x	y	z	$U_{\rm eq}$(Å^2)
Molecule 1				
S(101)	0·1775 (2)	0·0817 (1)	0·40041 (4)	0·0491 (5)
O(101)	0·3462 (5)	0·0222 (3)	0·3791 (1)	0·063 (1)
O(102)	0·1891 (5)	0·1965 (3)	0·4201 (1)	0·060 (1)
O(103)	−0·9039 (6)	0·3202 (4)	0·0819 (1)	0·093 (2)
O(104)	−0·6686 (6)	0·4312 (3)	0·0277 (1)	0·083 (2)
O(105)	−0·3741 (7)	0·4238 (4)	0·0506 (1)	0·085 (2)
N(101)	0·0379 (5)	−0·1673 (3)	0·4817 (1)	0·042 (2)
N(102)	0·0883 (5)	0·0051 (3)	0·4421 (1)	0·044 (2)
N(103)	−0·3792 (6)	0·1814 (3)	0·2483 (1)	0·052 (2)
N(104)	−0·3288 (6)	0·2241 (3)	0·2090 (1)	0·055 (2)
C(101)	0·0942 (6)	−0·1145 (5)	0·4403 (2)	0·043 (2)
C(102)	0·1489 (7)	−0·1919 (5)	0·4028 (2)	0·054 (2)
C(103)	0·1420 (7)	−0·3120 (5)	0·4097 (2)	0·060 (2)
C(104)	0·0856 (7)	−0·3602 (5)	0·4529 (2)	0·059 (2)
C(105)	0·0323 (7)	−0·2868 (5)	0·4882 (2)	0·053 (2)
C(106)	0·0126 (7)	0·1058 (4)	0·3544 (2)	0·040 (2)
C(107)	0·0748 (7)	0·1497 (4)	0·3108 (2)	0·056 (2)
C(108)	−0·0520 (8)	0·1780 (4)	0·2751 (2)	0·060 (2)
C(109)	−0·2373 (8)	0·1581 (4)	0·2824 (2)	0·045 (2)
C(110)	−0·2954 (7)	0·1138 (4)	0·3261 (2)	0·045 (2)
C(111)	−0·1711 (7)	0·0884 (4)	0·3622 (2)	0·042 (2)
C(112)	−0·4782 (8)	0·2478 (4)	0·1766 (2)	0·051 (2)
C(113)	−0·4411 (8)	0·3041 (4)	0·1339 (2)	0·055 (2)
C(114)	−0·5806 (9)	0·3323 (4)	0·1011 (2)	0·054 (2)
C(115)	−0·7578 (9)	0·3000 (5)	0·1109 (2)	0·066 (3)
C(116)	−0·7951 (8)	0·2421 (5)	0·1543 (2)	0·071 (3)
C(117)	−0·6557 (9)	0·2162 (5)	0·1866 (2)	0·063 (2)
C(118)	−0·5475 (11)	0·3995 (5)	0·0564 (2)	0·069 (3)
Molecule 2				
S(201)	0·7088 (2)	0·4107 (1)	0·40500 (4)	0·0485 (5)
O(201)	0·8881 (4)	0·4454 (3)	0·3900 (1)	0·056 (1)
O(202)	0·7009 (5)	0·2905 (2)	0·42412 (9)	0·055 (1)
O(203)	−0·2962 (7)	0·6710 (4)	0·0749 (2)	0·109 (2)
O(204)	−0·0295 (7)	0·7532 (4)	0·0238 (1)	0·123 (3)
O(205)	0·2547 (8)	0·7381 (5)	0·0529 (2)	0·119 (3)
N(201)	0·5389 (5)	0·6667 (3)	0·4835 (1)	0·042 (2)
N(202)	0·6054 (5)	0·4931 (3)	0·4454 (1)	0·044 (1)
N(203)	0·1838 (6)	0·4863 (4)	0·2453 (2)	0·070 (2)
N(204)	0·2423 (7)	0·5309 (4)	0·2083 (2)	0·070 (2)
C(201)	0·6058 (6)	0·6127 (4)	0·4430 (2)	0·041 (2)
C(202)	0·6574 (7)	0·6890 (5)	0·4055 (2)	0·048 (2)
C(203)	0·6434 (7)	0·8101 (4)	0·4113 (2)	0·049 (2)
C(204)	0·5799 (7)	0·8583 (4)	0·4538 (2)	0·050 (2)
C(205)	0·5287 (7)	0·7849 (5)	0·4897 (2)	0·048 (2)
C(206)	0·5638 (8)	0·4297 (4)	0·3553 (2)	0·043 (2)
C(207)	0·6276 (7)	0·4725 (4)	0·3122 (2)	0·058 (2)
C(208)	0·5087 (9)	0·4908 (5)	0·2746 (2)	0·064 (3)
C(209)	0·3259 (9)	0·4655 (5)	0·2807 (2)	0·055 (2)
C(210)	0·2629 (8)	0·4208 (4)	0·3238 (2)	0·059 (2)
C(211)	0·3812 (8)	0·4034 (4)	0·3613 (2)	0·053 (2)
C(212)	0·0986 (10)	0·5595 (5)	0·1740 (2)	0·068 (3)
C(213)	0·1533 (9)	0·6169 (5)	0·1334 (2)	0·072 (3)
C(214)	0·0248 (11)	0·6547 (5)	0·0985 (2)	0·072 (3)
C(215)	−0·1590 (12)	0·6326 (6)	0·1060 (2)	0·081 (3)
C(216)	−0·2157 (9)	0·5725 (5)	0·1470 (2)	0·084 (3)
C(217)	−0·0868 (10)	0·5357 (5)	0·1808 (2)	0·076 (3)
C(218)	0·0812 (13)	0·7190 (6)	0·0552 (2)	0·091 (3)
DMF molecule				
O(1)	0·6454 (9)	0·1366 (5)	0·0165 (2)	0·155 (3)
N(1)	0·7284 (14)	0·0276 (6)	0·0824 (2)	0·136 (4)
C(1)	0·773 (2)	0·0996 (7)	0·0469 (3)	0·149 (5)
C(2)	0·875 (2)	−0·0046 (7)	0·1176 (3)	0·185 (6)
C(3)	0·546 (2)	−0·0159 (8)	0·0890 (3)	0·178 (6)

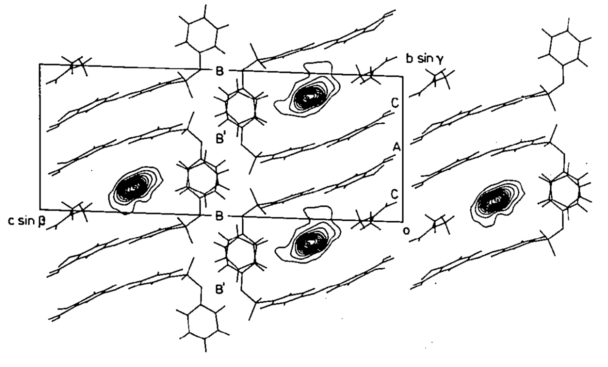

Fig. 1. Projection of the structure down the *a* axis, on which is superimposed the section at $x = \frac{1}{3}$ of the Fourier synthesis calculated from the continuous solvent contribution to the calculated structure factors. Contour levels at $0{\cdot}15\,\mathrm{e\,Å^{-3}}$. The positions of the three different hydrogen-bond schemes (*A*,*B*,*C*) are indicated.

Discussion. The triclinic unit cell contains four molecules of salazopyrine, two molecules of DMF and two solvent channels (see below) as shown in Fig. 1. The molecular structure with labelling and hydrogen bonds is depicted in Fig. 2. Bond distances and bond angles are listed in Table 2. The two crystallographically independent salazopyrine molecules differ mainly in the value of the torsion angles about the S—C bonds (data for molecule 2 are in brackets): N(102)—S(101)—C(106)—C(111) = 16·1 (4)° [57·7 (4)°], and the sign of the torsion angles about the S—N bonds C(106)—S(101)—N(102)—C(101) = 81·3 (4)° [−75·8 (4)°]. This indicates that the crystal lattice plays a rôle in determining the molecular conformation in the crystal. These dihedral angles for molecule 2 are similar to those reported earlier for the related sulfapyridine molecules (Basak, Chaudhuri & Mazumdar, 1984; Bar & Bernstein, 1985; Bernstein, 1988). The conformation of aryl—SO_2—N—C systems was studied by Kálmán, Czugler & Argay (1981). Unequivocal location of the H atoms on the pyridine N atoms for both salazopyrine molecules indicates that these molecules exist in the imide form, which is also found in the structures of the four reported modifications of sulfapyridine. The two azo-bridged phenyl rings in both salazopyrine molecules are almost coplanar {6·9 (2)°

---

* Lists of anisotropic thermal parameters, H-atom positions, bond angles and distances involving H atoms, torsion angles and a list of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52589 (32 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

[10·5 (3)°]}, indicating extensive conjugation. This was expected because of the orange colour of the compound.

Hydrogen bonding. The two independent salazopyrine molecules and the DMF molecule join *via* hydrogen bonds into two separate hydrogen-bonded aggregates involving three hydrogen-bond schemes (Figs. 1, 2). Molecule 1 links on both ends across inversion centres, *via* schemes *A* and *B* respectively, into an infinite chain running in the [1$\bar{1}$1] direction. In scheme *A* the hydroxyl H atom is intramolecularly bridged to the neighbouring carboxyl group which forms by itself a cyclic dimer across an inversion centre. Such cyclic dimers are commonly observed in structures of dicarboxylic acids (van der Sluis & Kroon, 1985). Scheme *A* is also found in the structure of *p*-aminosalicylic acid (Bertinotti, Giacomello & Liquori, 1954). In scheme *B* the H atom of the pyridine nitrogen forms a cyclic bifurcated hydrogen-bond system over an inversion centre with the imide N and the sulfonyl O atom as acceptor atoms. Molecule 2 dimerizes on one side across an inversion centre (scheme *B*′), but further aggregation stops on the carboxyl side with a DMF molecule in an arrangement resembling a carboxyl dimer (scheme *C*). Data on the hydrogen-bond geometry are summarized in Table 2.

Continuous electron density channel. Three different solvents are potential candidates for the explanation of the observed electron density in the channel. Ethanol was used in the isolation and water and DMF have been used in the crystallization. NMR data (^{1}H NMR, 500 MHz, in DMSO-d_6) indicate approximately one DMF molecule per asymmetric unit, but do not support the presence of ethanol. A substantial amount of water was found, which, however, gives no definite proof for its presence in the crystal. It was concluded that the channel

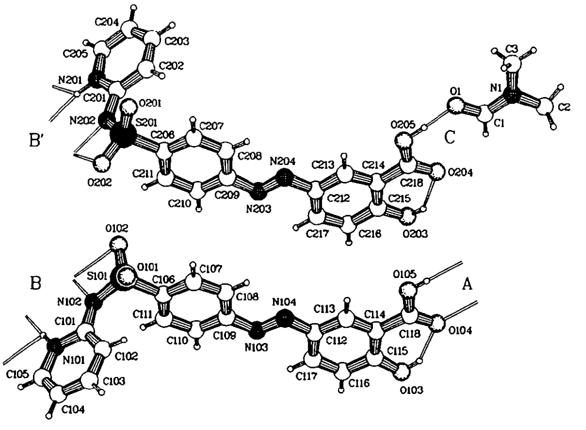

Fig. 2. *PLUTON* drawing of the molecular structure with adopted labelling. Atomic labels of the type *Xijk*, with *i* = 1,2 refering to molecule 1 and 2 respectively. *A*, *B* and *C* denote the hydrogen-bond schemes.

Table 2. *Bond distances* (Å), *bond angles* (°) *and hydrogen-bond geometry with e.s.d.'s in parentheses*

O(101)—S(101)	1·437 (4)	N(103)—C(109)	1·422 (7)	C(108)—C(109)	1·388 (8)
O(102)—S(101)	1·443 (4)	N(104)—C(112)	1·429 (7)	C(109)—C(110)	1·384 (7)
O(103)—C(115)	1·348 (7)	C(101)—C(102)	1·413 (7)	C(110)—C(111)	1·378 (7)
O(104)—C(118)	1·224 (8)	C(102)—C(103)	1·369 (8)	C(112)—C(113)	1·374 (6)
O(105)—C(118)	1·315 (9)	C(103)—C(104)	1·384 (8)	C(112)—C(117)	1·386 (9)
N(101)—C(101)	1·361 (6)	C(104)—C(105)	1·336 (8)	C(113)—C(114)	1·389 (8)
N(101)—C(105)	1·360 (7)	C(106)—C(107)	1·390 (6)	C(114)—C(115)	1·386 (9)
N(102)—C(101)	1·348 (7)	C(106)—C(111)	1·371 (7)	C(114)—C(118)	1·474 (7)
N(102)—S(101)	1·597 (4)	C(106)—S(101)	1·780 (5)	C(115)—C(116)	1·398 (7)
N(103)—N(104)	1·253 (6)	C(107)—C(108)	1·385 (7)	C(116)—C(117)	1·377 (8)
O(201)—S(201)	1·440 (3)	N(203)—C(209)	1·448 (7)	C(208)—C(209)	1·385 (9)
O(202)—S(201)	1·447 (3)	N(204)—C(212)	1·441 (8)	C(209)—C(210)	1·382 (8)
O(203)—C(215)	1·364 (9)	C(201)—C(202)	1·408 (7)	C(210)—C(211)	1·376 (8)
O(204)—C(218)	1·231 (9)	C(202)—C(203)	1·374 (7)	C(212)—C(213)	1·364 (8)
O(205)—C(218)	1·294 (11)	C(203)—C(204)	1·375 (7)	C(212)—C(217)	1·400 (10)
N(201)—C(201)	1·360 (6)	C(204)—C(205)	1·354 (7)	C(213)—C(214)	1·394 (9)
N(201)—C(205)	1·345 (7)	C(206)—C(207)	1·377 (7)	C(214)—C(215)	1·385 (12)
N(202)—C(201)	1·349 (6)	C(206)—C(211)	1·387 (8)	C(214)—C(218)	1·467 (9)
N(202)—S(201)	1·602 (4)	C(206)—S(201)	1·768 (5)	C(215)—C(216)	1·392 (8)
N(203)—N(204)	1·223 (7)	C(207)—C(208)	1·379 (8)	C(216)—C(217)	1·372 (9)
O(1)—C(1)	1·298 (12)	N(1)—C(2)	1·476 (13)	N(1)—C(1)	1·320 (11)
N(1)—C(3)	1·460 (14)				

C(101)—N(101)—C(105)	124·1 (4)	N(104)—C(112)—C(113)	117·6 (5)
C(101)—N(102)—S(101)	121·6 (3)	N(104)—C(112)—C(117)	122·9 (4)
N(104)—N(103)—C(109)	115·7 (4)	C(113)—C(112)—C(117)	119·5 (5)
N(103)—N(104)—C(112)	113·0 (4)	C(112)—C(113)—C(114)	120·7 (5)
N(101)—C(101)—N(102)	113·6 (4)	C(113)—C(114)—C(115)	119·8 (5)
N(101)—C(101)—C(102)	116·0 (5)	C(113)—C(114)—C(118)	121·7 (6)
N(102)—C(101)—C(102)	130·4 (4)	C(115)—C(114)—C(118)	118·4 (5)
C(101)—C(102)—C(103)	119·5 (5)	O(103)—C(115)—C(114)	125·6 (5)
C(102)—C(103)—C(104)	121·6 (5)	O(103)—C(115)—C(116)	115·0 (5)
C(103)—C(104)—C(105)	118·8 (5)	C(114)—C(115)—C(116)	119·4 (5)
N(101)—C(105)—C(104)	120·0 (5)	C(115)—C(116)—C(117)	120·0 (5)
C(107)—C(106)—C(111)	120·9 (4)	C(112)—C(117)—C(116)	120·5 (5)
C(107)—C(106)—S(101)	117·3 (4)	O(104)—C(118)—O(105)	122·9 (5)
C(111)—C(106)—S(101)	121·7 (3)	O(104)—C(118)—C(114)	123·9 (7)
C(106)—C(107)—C(108)	119·2 (5)	O(105)—C(118)—C(114)	113·2 (6)
C(107)—C(108)—C(109)	120·2 (4)	O(101)—S(101)—O(102)	116·8 (2)
N(103)—C(109)—C(108)	125·4 (4)	O(101)—S(101)—N(102)	113·9 (2)
N(103)—C(109)—C(110)	115·2 (5)	O(101)—S(101)—C(106)	106·1 (2)
C(108)—C(109)—C(110)	119·3 (5)	O(102)—S(101)—N(102)	105·2 (2)
C(109)—C(110)—C(111)	120·8 (5)	O(102)—S(101)—C(106)	106·8 (2)
C(106)—C(111)—C(110)	119·5 (4)	N(102)—S(101)—C(106)	107·5 (2)
C(201)—N(201)—C(205)	123·9 (4)	N(204)—C(212)—C(213)	115·0 (6)
C(201)—N(202)—S(201)	120·9 (3)	N(204)—C(212)—C(217)	124·5 (5)
N(204)—N(203)—C(209)	112·2 (5)	C(213)—C(212)—C(217)	120·5 (6)
N(203)—N(204)—C(212)	112·6 (5)	C(212)—C(213)—C(214)	120·5 (6)
N(201)—C(201)—N(202)	113·2 (4)	C(213)—C(214)—C(215)	118·6 (5)
N(201)—C(201)—C(202)	116·1 (4)	C(213)—C(214)—C(218)	121·0 (7)
N(202)—C(201)—C(202)	130·7 (4)	C(215)—C(214)—C(218)	120·5 (6)
C(201)—C(202)—C(203)	120·2 (4)	O(203)—C(215)—C(214)	122·7 (5)
C(202)—C(203)—C(204)	120·6 (4)	O(203)—C(215)—C(216)	115·9 (7)
C(203)—C(204)—C(205)	119·1 (4)	C(214)—C(215)—C(216)	121·4 (6)
N(201)—C(205)—C(204)	120·1 (4)	C(215)—C(216)—C(217)	119·1 (6)
C(207)—C(206)—C(211)	120·6 (5)	C(212)—C(217)—C(216)	119·9 (5)
C(207)—C(206)—S(201)	121·3 (4)	O(204)—C(218)—O(205)	122·8 (6)
C(211)—C(206)—S(201)	118·1 (3)	O(204)—C(218)—C(214)	122·2 (8)
C(206)—C(207)—C(208)	119·9 (5)	O(205)—C(218)—C(214)	114·9 (6)
C(207)—C(208)—C(209)	119·6 (5)	O(201)—S(201)—O(202)	118·6 (2)
N(203)—C(209)—C(208)	125·5 (5)	O(201)—S(201)—N(202)	112·9 (2)
N(203)—C(209)—C(210)	114·0 (5)	O(201)—S(201)—C(206)	107·5 (2)
C(208)—C(209)—C(210)	120·4 (5)	O(202)—S(201)—N(202)	103·5 (2)
C(209)—C(210)—C(211)	119·9 (5)	O(202)—S(201)—C(206)	107·0 (2)
C(206)—C(211)—C(210)	119·6 (5)	N(202)—S(201)—C(206)	106·6 (2)
C(1)—N(1)—C(2)	115·6 (9)	C(2)—N(1)—C(3)	120·2 (7)
C(1)—N(1)—C(3)	124·2 (8)	O(1)—C(1)—N(1)	118·1 (10)

D—H···*A*	*D*···*A* (Å)	*D*—H (Å)	H···*A* (Å)	*D*—H···*A* (°)
N(101)—H(105)···O(102)^{i}	3·192 (5)	0·980 (5)	2·589 (5)	119·8 (3)
N(101)—H(105)···N(102)^{i}	2·922 (5)	0·980 (5)	1·944 (5)	175·6 (4)
O(103)—H(113)···O(104)	2·642 (6)	0·870 (40)	1·870 (50)	147·0 (40)
O(105)—H(114)···O(104)^{ii}	2·726 (5)	0·800 (40)	1·920 (40)	179·0 (50)
N(201)—H(205)···O(202)^{iii}	3·092 (5)	0·981 (5)	2·486 (5)	119·7 (3)
N(201)—H(205)···N(202)^{iii}	2·896 (5)	0·981 (5)	1·922 (5)	171·8 (4)
O(203)—H(213)···O(204)	2·601 (7)	0·890 (50)	1·830 (50)	143·0 (40)
O(205)—H(214)···O(1)^{iv}	2·507 (7)	0·990 (50)	1·530 (50)	171·0 (40)

Symmetry codes: (i) $-x, -y, -z+1$; (ii) $-x-1, -y+1, -z$; (iii) $-x+1, -y+1, -z+1$; (iv) $-x+1, -y+1, -z$.

is most probably filled with disordered water. The electron count in the solvent channel, as obtained with the *BYPASS* procedure (van der Sluis & Spek, 1990), yielded 90·0 electrons which is equivalent to 4·5 water molecules in the asymmetric unit. The corresponding calculated density of 1·39 Mg m^{-3} is in agreement with the experimental ρ_{obs} = 1·36 (2) Mg m^{-3}. The hydrophobic nature of the interior of the channel may be the cause for the disorder of the water molecules. The nearly continuous density observed suggests a possible incommensurate ordering of the water molecules in the channel.

We thank A. J. M. Duisenberg for collecting the X-ray data.

References

Bar, I. & Bernstein, J. (1985). *J. Pharm. Sci.* **74**, 255–263.
Basak, A. K., Chaudhuri, S. & Mazumdar, S. K. (1984). *Acta Cryst.* **C40**, 1848–1851.
Bernstein, J. (1988). *Acta Cryst.* **C44**, 900–902.
Bertinotti, F., Giacomello, G. & Liquori, A. M. (1954). *Acta Cryst.* **7**, 808–812.
Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
Kálmán, A., Czugler, M. & Argay, Gy. (1981). *Acta Cryst.* **B37**, 868–877.
McCandlish, L. E., Stout, G. H. & Andrews, L. C. (1975). *Acta Cryst.* **A31**, 245–249.
McPherson, A. Jr (1976). In *Methods of Biochemical Analysis*, Vol. 23, edited by D. Glick, p. 277. New York: Wiley–Interscience.
Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
Sheldrick, G. M. (1986). *SHELXS86*. Program for crystal structure solution. Univ. of Göttingen, Federal Republic of Germany.
Sluis, P. van der & Kroon, J. (1985). *Acta Cryst.* **C41**, 956–959.
Sluis, P. van der & Kroon, J. (1989). *J. Cryst. Growth*, **97**, 645–656.
Sluis, P. van der & Spek, A. L. (1990). *Acta Cryst.* **A46**, 194–201.
Spek, A. L. (1982). *The EUCLID package*. In *Computational Crystallography*, edited by D. Sayre, p. 528. Oxford: Clarendon Press.
The Merck Index (1983). 10th edition, p. 1283. Rahway, NJ: Merck & Co.

Acta Cryst. (1990). **C46**, 886–888

Structure of Ethyl 2,4,4,6,6-Pentachloro-1,3,5,2λ^5,4λ^5,6λ^5-triazatriphosphinine-2-carbamate

By A. Meetsma, P. L. Buwalda and J. C. van de Grampel*

Laboratory of Polymer Chemistry, University of Groningen, Nijenborgh 16, 9747 *AG Groningen, The Netherlands*

(*Received* 21 *June* 1989; *accepted* 4 *September* 1989)

Abstract. $C_3H_6Cl_5N_4O_2P_3$, $M_r = 400·29$, orthorhombic, *Pnnm*, $a = 9·195\,(2)$, $b = 14·348\,(3)$, $c = 11·351\,(1)$ Å, $V = 1497·5\,(5)$ Å^3, $Z = 4$, $D_x = 1·775$ g cm^{-3}, $\lambda(\text{Mo } K\bar{\alpha}) = 0·71073$ Å, $\mu = 12·8$ cm^{-1}, $F(000) = 792$, $T = 298$ K, $R_F = 0·042$ for 1035 reflections with $I \geq 2·5\sigma(I)$. The crystal structure consists of dimers arising from hydrogen-bond bridges. The organic moiety is located close to the NP ring. The endocyclic N—P bond lengths average to 1·570 (5) Å; N—P (exocyclic) = 1·662 (6) Å. The P—Cl bond lengths vary from 1·974 (2) to 2·007 (3) Å.

Introduction. Although for reactions of $(NPCl_2)_3$ with alkali metal cyanates hardly any product formation is observed, addition of one or more equivalents of alcohol to these reaction mixtures leads to high yields of the corresponding carbamato derivatives (Buwalda, 1989; van de Grampel, Buwalda, van der Huizen, Wilting, Meetsma & van Bolhuis, 1987). In that way the title compound could be prepared in 80% yield from a 1:1:1 mixture of $(NPCl_2)_3$, NaOCN, and ethanol in dry acetonitrile. In order to examine the position of the organic group with respect to the inorganic ring, and its influence on the endocyclic bonding, a structure determination by X-rays was carried out.

Experimental. Transparent, colourless, needle-shaped crystals were obtained by recrystallization from petroleum ether 60–80. A block-shaped fragment (0·23 × 0·25 × 0·30 mm) cleaved from a larger crystal was glued on the top of a glass fibre. Enraf–Nonius CAD-4F diffractometer was interfaced to a Micro-

---

* Author to whom correspondence should be addressed.

0108-2701/90/050886-03$03.00 © 1990 International Union of Crystallography