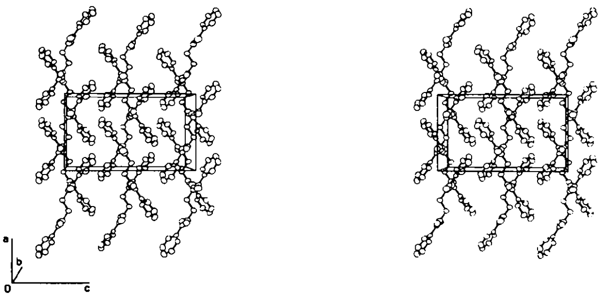

Fig. 5. Organisation des molécules dans le cristal.

4. Il est très probable que l'effet stabilisateur des nombreux ponts hydrogène joue un rôle prépondérant et que si l'énergie due à ces ponts hydrogène avait été incorporée dans les calculs d'analyse conformationnelle, le minimum n° (V) aurait vu son énergie s'abaisser de manière significative.

Il n'existe pas de contacts intermoléculaires courts autres que les ponts hydrogène décrits ci-dessus. L'arrangement en chevron typique de ces molécules est représenté à la Fig. 5.

Les auteurs tiennent à remercier le Ministère de l'Education de la Province de Québec pour l'aide financière apportée à ce travail.

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# The Structure of the Imidazolium Salt of *trans*-2-Hydroxy-4,5-dimethyl-1,3,2-dioxaphospholane 2-Sulphide Monohydrate*

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## Abstract

$C_7H_{13}N_2O_3PS.H_2O$ crystallizes in the triclinic system, $a = 7{\cdot}239\,(1)$, $b = 13{\cdot}044\,(2)$, $c = 6{\cdot}802\,(1)$ Å, $\alpha = 100{\cdot}42\,(1)$, $\beta = 73{\cdot}33\,(1)$, $\gamma = 98{\cdot}64\,(1)°$, $V = 601{\cdot}8$ Å$^3$, $D_m = 1{\cdot}38$, $D_c = 1{\cdot}4$ Mg m$^{-3}$, $Z = 2$, $\mu(\mathrm{Cu}\ K\alpha) = 3{\cdot}51$ mm$^{-1}$, space group $P\bar{1}$. The structure was refined to $R = 0{\cdot}04$. The five-membered ring in the title compound has the envelope conformation with the C(1) atom in the flap position. The asymmetry parameters are $\Delta C_s^{C(1)} = 8{\cdot}2$ and $\Delta C_2^{P} = 8{\cdot}9°$. The geometry and conformation of three diastereoisomeric

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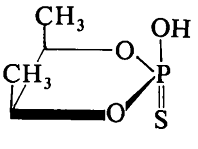
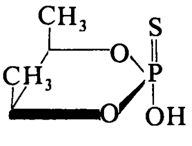
forms of 2-hydroxy-4,5-dimethyl-1,3,2-dioxaphospholane 2-sulphide are compared and briefly discussed.

## Introduction

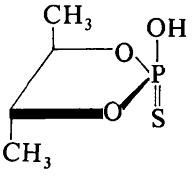
2-Hydroxy-4,5-dimethyl-1,3,2-dioxaphospholane 2-sulphide (I) can exist in the three diastereoisomeric forms shown below.



*trans*-I



*cis*-I



(±)-I

In a previous paper of this series (Mikołajczyk & Witczak, 1977) we described the stereospecific synthesis of these isomers which have been characterized as crystalline imidazolium salts. The geometry of the *cis* and *trans* pair of (I) derived from *meso*-2,3-butanediol was established by means of chemical correlation and NMR spectral studies. In the present paper we report the results of the X-ray analysis of the imidazolium salt of *trans*-I which was undertaken in order to confirm our configurational assignment.

## Experimental

The imidazolium salt of *trans*-2-hydroxy-4,5-dimethyl-1,3,2-dioxaphospholane 2-sulphide (I) crystallizes with one molecule of water in the form of prisms. Cell dimensions were obtained from a crystal shaped into a sphere of diameter 0·3 mm by least-squares fit of the settings for 15 reflexions (±*hkl*) on a Syntex $P2_1$ diffractometer (Cu $K\alpha$, $\lambda = 1\cdot54178$ Å). Intensity data were collected in the $\theta$–$2\theta$ mode ($3\cdot0 < 2\theta < 114°$) with graphite-monochromated Cu $K\alpha$ radiation. A Lorentz–polarization correction but no absorption correction was applied. After application of the acceptance criterion $F < 4\sigma(F)$, 1531 from 1581 unique measured reflexions were considered to be observed. The structure was solved by the automatic centrosymmetric direct method *SHELX*-76 (Sheldrick, 1976) and refined by a full-matrix least-squares method with anisotropic temperature factors for all non-hydrogen atoms. The difference Fourier syntheses revealed the positions of the O atom of the water and the H atoms. The final $R = 0\cdot04$ and $R_w = (\sum w^{1/2}\Delta/\sum w^{1/2}|F_o|) = 0\cdot050$; the weights were given by $w = k[\sigma^2(F_o) + gF_o^2]^{-1}$. Complex neutral-atom scattering factors were employed (Cromer & Waber, 1965; Cromer & Liberman, 1970).

## Discussion

A perspective view of the molecule of *trans*-I with the numbering of atoms is shown in Fig. 1 while the packing of *trans*-I in the unit cell is presented in Fig. 2. Tables 1 and 2 give the final positional parameters.* The 1,3,2-dioxaphospholane ring in *trans*-I has the open-envelope conformation with the C(1) atom in the flap position. This atom is 0·557 (3) Å above the plane passing through the atoms P, O(2), O(3) and C(2). The

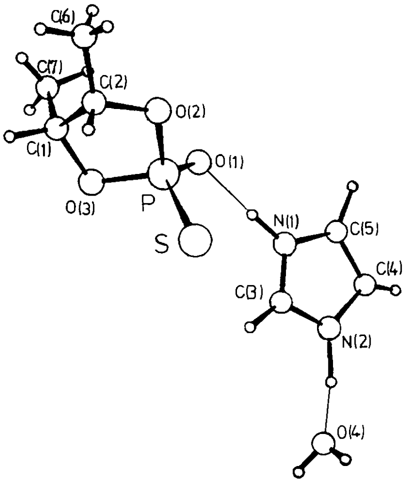


Fig. 1. A perspective view of the molecule of *trans*-I.

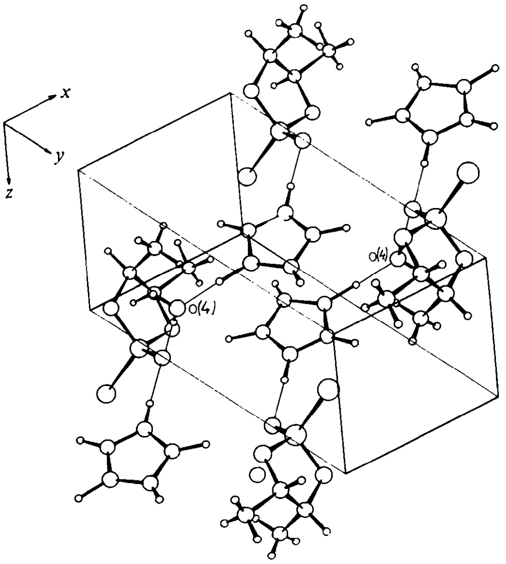


Fig. 2. The packing of *trans*-I in the unit cell.

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* Lists of structure factors, anisotropic thermal parameters and bond lengths involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35059 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters for the non-hydrogen atoms*

| | *x* | *y* | *z* |
|---|---|---|---|
| P(1) | 0·9582 (1) | 0·2196 (1) | −0·0049 (1) |
| S(1) | 0·7751 (1) | 0·1880 (1) | 0·2563 (1) |
| O(1) | 0·9424 (3) | 0·3219 (1) | −0·0663 (3) |
| O(2) | 0·9467 (2) | 0·1243 (1) | −0·1873 (3) |
| O(3) | 1·1806 (2) | 0·2153 (1) | −0·0111 (3) |
| C(1) | 1·2417 (4) | 0·1137 (2) | −0·1202 (4) |
| C(2) | 1·1376 (4) | 0·0884 (2) | −0·2907 (5) |
| C(7) | 1·4610 (5) | 0·1220 (3) | −0·1883 (6) |
| C(6) | 1·2280 (5) | 0·1417 (3) | −0·4803 (5) |
| O(4) | 0·9841 (2) | 0·3752 (1) | 0·5395 (3) |
| N(1) | 0·6361 (3) | 0·4262 (1) | 0·1547 (3) |
| N(2) | 0·3450 (3) | 0·4579 (2) | 0·3186 (3) |
| C(5) | 0·6347 (3) | 0·5324 (2) | 0·1858 (3) |
| C(4) | 0·4512 (4) | 0·5526 (2) | 0·2910 (4) |
| C(3) | 0·4594 (3) | 0·3827 (2) | 0·2358 (4) |

Table 2. *Positional parameters for the hydrogen atoms*

| | *x* | *y* | *z* | *U* (Å$^2$) |
|---|---|---|---|---|
| H(1) | 0·749 (5) | 0·383 (3) | 0·082 (5) | 0·050 (9) |
| H(2) | 0·182 (6) | 0·428 (4) | 0·398 (8) | 0·086 (13) |
| H(3) | 0·925 (7) | 0·318 (4) | 0·474 (8) | 0·092 (14) |
| H(4) | 0·979 (6) | 0·356 (3) | 0·661 (7) | 0·080 (13) |
| H(5) | 0·760 (5) | 0·592 (3) | 0·137 (5) | 0·049 (8) |
| H(6) | 0·404 (6) | 0·616 (3) | 0·306 (7) | 0·070 (13) |
| H(7) | 0·410 (7) | 0·304 (4) | 0·254 (8) | 0·098 (14) |
| H(11) | 1·184 (5) | 0·062 (3) | −0·022 (5) | 0·036 (8) |
| H(71) | 1·511 (4) | 0·181 (2) | −0·293 (5) | 0·042 (7) |
| H(22) | 1·138 (7) | 0·006 (3) | −0·352 (7) | 0·045 (7) |
| H(72) | 1·513 (7) | 0·126 (4) | −0·054 (8) | 0·079 (15) |
| H(73) | 1·507 (8) | 0·053 (6) | −0·263 (10) | 0·110 (17) |
| H(61) | 1·252 (5) | 0·222 (3) | −0·449 (6) | 0·049 (10) |
| H(62) | 1·337 (8) | 0·113 (4) | −0·550 (8) | 0·100 (15) |
| H(63) | 1·139 (7) | 0·136 (4) | −0·579 (7) | 0·080 (12) |

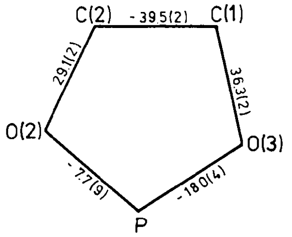

Fig. 3. Torsion angles in the dioxaphospholane ring (°) with e.s.d.'s in parentheses.

torsion angles in the dioxaphospholane ring are given in Fig. 3. The corresponding asymmetry parameters (Duax & Norton, 1975; Altona, Geise & Romers, 1968) are $\Delta C_s^{C(1)} = 8{\cdot}2$, $\Delta C_2^{P} = 8{\cdot}9°$. The imidazolium cation has two N atoms which may take part in hydrogen bonds with the O(1) atom of the monothiophosphate anion and the O(4) atom of the water molecule.

The hydrogen bonds stabilize the crystal lattice. The linking of the imidazolium cations with the cyclic monothiophosphate anions through the hydrogen bonds creates the chains along the shortest cell axis. In the structure of *trans*-I, three hydrogen bonds are observed: O(4)···N(2) = 2·781 (4), O(1)···N(1) = 2·698 (4), O(1)···O(4) = 2·812 (4) Å. The dihedral angle between the plane of the imidazole ring and the plane defined by the atoms P, O(2), O(3), C(1) and C(2) is 56·4 (5)°.

It is convenient to discuss the results of the X-ray analysis of *trans*-I together with the structural parameters for *cis*-I (Wieczorek, 1980) and (±)-I (Wieczorek, Karolak-Wojciechowska, Goliński, Bartczak, Mikołajczyk & Witczak, 1976) in order to illustrate the influence of the configuration of the dioxaphospholane ring on its conformation.

The bond lengths and angles for *trans*-I are listed in Tables 3 and 4.

The analysis of the analogous bond distances and angles in the dioxaphospholane ring of the three diastereoisomeric forms of I shows that different situations of the exocyclic methyl groups give rise to significantly different bond distances and angles as well as to a deformation of the five-membered ring. Some detailed information about the geometry of exocyclic substituents ($CH_3$, S, O) in the dioxaphospholane ring is given in Table 5. The P=S bond is axially situated with respect to the dioxaphospholane ring PO(3)-C(1)C(2)O(2) with an angle between the bond and the mean plane of the ring of −51·7 (0·7), −58·8 (0·2), −50·1 (0·4) and −53·2 (0·4)° for (±)-I, *trans*-I and two conformations of *cis*-I, respectively. Thus, the angle is biggest for the isomer with a *trans* relationship

Table 3. *Bond lengths* (Å)

| | | | |
|---|---|---|---|
| S(1)–P(1) | 1·958 (1) | C(7)–C(1) | 1·514 (4) |
| O(1)–P(1) | 1·497 (2) | C(6)–C(2) | 1·510 (4) |
| O(2)–P(1) | 1·601 (2) | C(5)–N(1) | 1·364 (3) |
| O(3)–P(1) | 1·608 (2) | C(3)–N(1) | 1·324 (3) |
| C(2)–O(2) | 1·463 (3) | C(4)–N(2) | 1·367 (3) |
| C(1)–O(3) | 1·461 (3) | C(3)–N(2) | 1·319 (3) |
| C(2)–C(1) | 1·520 (5) | C(4)–C(5) | 1·355 (3) |

Table 4. *Bond angles* (°)

| | | | |
|---|---|---|---|
| O(1)–P(1)–S(1) | 115·1 (1) | C(7)–C(1)–C(2) | 116·8 (2) |
| O(2)–P(1)–S(1) | 110·5 (1) | C(1)–C(2)–O(2) | 103·1 (2) |
| O(2)–P(1)–O(1) | 111·5 (1) | C(6)–C(2)–O(2) | 109·1 (3) |
| O(3)–P(1)–S(1) | 113·3 (1) | C(6)–C(2)–C(1) | 116·2 (2) |
| O(3)–P(1)–O(1) | 108·2 (1) | C(3)–N(1)–C(5) | 108·9 (2) |
| O(3)–P(1)–O(2) | 96·8 (1) | C(3)–N(2)–C(4) | 108·9 (2) |
| C(2)–O(2)–P(1) | 111·4 (2) | C(4)–C(5)–N(1) | 106·8 (2) |
| C(1)–O(3)–P(1) | 109·3 (2) | C(5)–C(4)–N(2) | 106·8 (2) |
| C(2)–C(1)–O(3) | 103·7 (2) | N(2)–C(3)–N(1) | 108·5 (2) |
| C(7)–C(1)–O(3) | 108·9 (2) | | |

Table 5. *Geometry of substituents in structures* (±)-I, *trans*-I *and cis*-I

| Compound | | Position relative to the phospholane ring PO(3)C(1)C(2)O(2) | Angle (°)* | | Position relative to sulphur |
|---|---|---|---|---|---|
| (±)-I | C(6) | equatorial | 27·4 (2·4) | | *trans* |
| | C(7) | equatorial | −27·9 (2·0) | | *cis* |
| | S | axial | −51·7 (0·7) | | |
| | O(1) | axial | 63·7 (0·9) | | *trans* |
| *trans*-I | C(6) | equatorial | 23·3 (0·4) | | *trans* |
| | C(7) | axial | 75·8 (0·7) | | *trans* |
| | S | axial | −58·8 (0·2) | | |
| | O(1) | axial | 55·8 (0·3) | | *trans* |
| *cis*-I | C(6) | equatorial | −25·3 (1·5) | −23·0 (1·5) | *cis* |
| | C(7) | axial | −70·1 (1·0) | −76·6 (1·0) | *cis* |
| | S | axial | −50·1 (0·4) | −53·2 (0·4) | |
| | O(1) | axial | 65·7 (0·5) | 60·8 (0·5) | *trans* |

* This is the angle between the mean plane of the ring and the ring–substituent bond.

between the methyl groups and the S atom. The P=S bond is longest in both structures with one or two methyl groups *trans* to sulphur. The P=S distance for *trans*-I and (±)-I is 1·958 (1) and 1·954 (9) Å, respectively. For *cis*-I this distance is significantly shorter at 7$\sigma$ [1·936 (3) and 1·935 (4) Å for both molecules] while the identical non-bonded distance S···O(1) is maintained in all structures. The bonds in phospholane rings for these three structures are not very different.

The spatial position of the $CH_3$ groups does not essentially influence the value of the O—P—O ring angle. This angle is 95·7 (8) for (±)-I, 96·8 (1) for *trans*-I and 96·4 (3) and 96·8 (4)° for *cis*-I. The values are similar to those found for other five-membered-ring phosphates (Chiu & Lipscomb, 1969; Newton, Cox & Bertrand, 1966; Newton & Campbell, 1974; Saenger & Eckstein, 1970; Coulter, 1973; van der Helm, Washecheck, Burks & Ealick, 1976; Reddy & Saenger, 1978). The comparison of other ring angles is also of interest. The differences of the P—O—C angles in the ring are 5° (5$\sigma$) for (±)-I, 2° (20$\sigma$) for *trans*-I and only 1·2° (3$\sigma$) for *cis*-I. The differences in value of the O—C—C angle are 9 (5$\sigma$), 0·4 (2$\sigma$) and 1·8–2·3° (3$\sigma$) for (±)-I, *trans*-I and *cis*-I, respectively. This is a consequence of the different degree of the twisting of the dioxaphospholane ring and the deformation from ideal conformation of the ring.

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