# THE CRYSTAL AND ELECTRON STRUCTURE OF O-(2-CHLOROETHYL) -O-ISOBUTYL-O-(2-PHENYL-4-METHYLTHIO-3-OXO-2H- -PYRIDAZINE-5-YL) THIOPHOSPHATE

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The crystal structure of the title fungicide was solved by direct methods, using $\Sigma_2$ relationship and tangent formula. The structure refinement was made by full-matrix least-squares with aniso-tropic temperature factors to the final $R = 0.096$ for 1 486 significant reflexions. The compound crystallizes in the orthorhombic system, the space group Pccn. The lattice parameters are $a = 1.8719(9)$, $b = 3.0426(33)$, $c = 0.7616(2)$ nm and $Z = 8$. The intermolecular interactions of types C—H...Cl and C—H...O are observed between the centrosymmetrically related molecules in the crystal structure. The coordination polyhedron around phosphorus is between trigonal pyramid and tetrahedron. The planes of the phenyl and pyridazine rings are rotated through 70° each other. The electron structure was calculated by semiempirical CNDO/2 method. The cal-culations revealed the most negative net charges on S(2) and O(1). The value of Wiberg index $I_w = 1.08$ and the bond distance 0.149 nm show that the bond N(1)—C(5) is simple and is not involved in the conjugation.

The organophosphoric compounds have ranked among the most important sub-stances used for protection of plants already a quarter of a century. It concerns namely the contact and system insecticides[1]. Recently, the herbicide on basis of phosphoromethylglycine[2−4] has acquired a great practical importance. The specific mechanism of activity of this compound consists in its penetration through leaves and in the gradual destruction of the weed roots. Its great importance for the national economy lies in the killing the couch-grass (Agropyron repens) the spread of which cannot be successfully suppressed by the preparates known till now. From the ana-logical new preparates, OFUNACK (pyridaphenthion) is successfully used for the cultivation of rice as insecticide and acaricide, namely because of its low toxicity for the warm blooded animals. In the last years, the pyridazine-5-yl esters of thio-phosphoric acid have stand at the top of interest as insecticides, acaricides and namely

as fungicides against flour insect. These compounds have different mechanism of activity in dependance on the selectivity (insecticide and fungicide effect)[6-9]. Because the space arrangement of molecules and the intramolecular structure play a substantial role in the explanation of mechanism of the pesticide effect, the crystal and electron structure of newly developed thiophosphate fungicide (denoted as FUNG-P) is described in this paper in detail with the aim to find the relations between the structure of the molecule and its biological activity.

## EXPERIMENTAL

The thiophosphate fungicide FUNG-P (the title compound) was prepared by the following way. The methyl ethyl ketone solution of O-(2-chloroethyl)-O-izobutylchlorothiophosphate was added under the intensive stirring at the room temperature into the mixture of 2-phenyl-4-methylthio- -3-oxo-5-hydroxy-2H-pyridazine (0·051 mol) and potassium carbonate (0·051 mol) in methyl ethyl ketone. Then, the mixture was stirred two hours under the room temperature and after that four hours under the temperature 70—80°C. The course of the reaction was traced by the thin-layer chromatography on Silufol plates in the system: toluene–acetone (8 : 2). After the end of the reaction, the mixture was cooled down and 100 ml of toluene was added. Then, the mixture was washed twice by water and once by 5% solution of sodium hydrogen carbonate. After the separation of layers, the toluene solution was dried by anhydrous sodium sulphate and toluene was destilled out under the low pressure. The destillation residue was crystallized from cyclohexane. The white plate crystals with well developed edges and stable under the normal conditions were recrystallized from dichloroethane and n-hexane. The purity of the substance was confirmed by analysis. For $C_{17}H_{22}N_2O_4PS_2Cl$ (448·9) calculated: 45·48% C, 4·94% H, 6·24% N; found: 45·88% C, 4·87% H, 6·40% N. The density of the crystals $D_m = 1·379(6)$ Mg . . m$^{-3}$ was determined by flotation in $CCl_4$ and n-hexan under the room temperature. The calculated density, under the assumption of eight formula units in the unit cell, was $D_x = 1·375$ Mg . . m$^{-3}$. The crystal with dimensions 0·2 × 0·3 × 0·1 mm was used for the determination of the basic crystallographic data (Table I) and for the intensity measurement. The systematic extinctions $hk0 : h + k = 2n + 1$, $0kl : l = 2n + 1$ and $h0l : l = 2n + 1$ showed that the compound crystallizes in the space group Pccn (orthorhombic system)[10]. The preliminary estimates of the lattice parameters calculated from rotational and Weissenberg photographs were refined by the least-squares method from ten exactly centered reflexions with the four-circle diffractometer Syntex P2$_1$. The range of $\theta$ angles of reflexions used for the refinement of lattice parameters was 1·7—40·5°. The characteristic radiation CuK$_\alpha$, under the working conditions 50 kV, 20 mA monochromatized by Ni filter, was used for all measurements. The integral intensities were measured by $\omega : 2\theta$ scan on the same automatic four-circle diffractometer Syntex P2$_1$ equipped with the scintilation counter and analyzer of the pulse height. The scan speed 4·5°—29·3° min$^{-1}$ was determined automatically on the basis of the preliminary two second measurement of the intensity. The crystal was recentered after every 500 measured reflexions. The intensities of reference reflexions measured after every 500 reflexions showed no significant decrease. Integral intensities were measured in the range 0° < 2$\theta$ < 110°. From the total number of 2 238 measured independent reflexions, 1 486 were classified as observed according to the criterion $I < 1·96\sigma(I)$ and used for the structure solution and refinement. The intensities were corrected for the LP factor, but no correction for absorption was made.

Structure Solution and Refinement

The structure was solved by direct methods using $\Sigma_2$ relationship and tangent formula. The starting set containing 15 reflexions with E-values higher than 1·3 led to 4 096 permutations. The E-maps for four most probable solutions were calculated. One of the E-maps showed a cluster of atoms with a pseudomirror at $y = 0$. It was recognized that the cluster consists of two overlapping structures. The positions of 10 atoms (two S, one P, four O and three C atoms) were determined from this E-map. The positions of the other non-hydrogen atoms were found in the two following cycles on the weighted Fourier maps. All non-hydrogen atoms refined, in five cycles of full-matrix least-squares with isotropic temperature factors and the weighting scheme $w^{-1} = = \sigma^2(F) + 0.004 |F|^2$, to the value $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.146$. The function minimized was $\sum w(|F_o| - |F_c|)^2$. After the next two cycles of the refinement with anisotropic temperature factors of non-hydrogen atoms, the $R$ value lowered to 0·113. Then the positions of hydrogen atoms were calculated under the assumption of ideal $sp^3$ and $sp^2$ hybridization of carbon atoms. The final refinement was made using fixed isotropic temperature factors and fixed positions of hydrogen atoms. The temperature factor of each H-atom was fixed equal with the equivalent value for the anisotropically refined atom to which it is bonded. In the last six cycles of refinement the $R$ factor decreased to a value of 0·096, and $R_w = \sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2 = = 0.095$. The difference Fourier map of residual electron density, calculated without contribution of hydrogen atoms, does not contain maximal higher than 0·61 e nm$^{-3}$ which are not in the positions of hydrogen atoms.

The scattering curves of neutral atoms were taken from International Tables[11]. The fractional coordinates of hydrogen atoms fixed in their ideal $sp^3$ and $sp^2$ positions are given in Table II. The Table III summarizes the fractional coordinates of all non-hydrogen atoms. Anisotropical temperature coefficients are deposited at the first author. The intramolecular bond distances and valence angles are given in Table IV and Table V. All the calculations were made with XTL program system of the Syntex Co. and with NRC program system[12] on the computer EC 1 033.

Electron Structure Calculation

The electron structure of the molecule FUNG-P was calculated by the semiempirical quantum-chemistry method CNDO/2[13,14]. The program GEOMO[15], which takes into account explicitly also the $d$-orbitals of phosphorus and sulphur atoms, was used. The calculations were directed to the partial optimalization of selected torsion angles $\varphi$, $\theta$, $\psi$, $\omega$ and to the calculation of indices characterizing the distribution of electron density. The optimization of molecular geometry enabled to gain the most stable conformations of the molecule and also the values of the energy bariers between individual conformations. Quantum-chemical calculation also provides data describing the distribution of electron density in the molecule, the character of individual bonds and the energies of molecular orbitals.

## STRUCTURE DESCRIPTION AND DISCUSSION

The positions of molecules of fungicide FUNG-P in the unit cell and the numbering of atoms are given in Fig. 1 and 2. The projection is along $c$ axes. All the atoms of FUNG-P lie in general positions. The crystal structure consits of non-centrosymmetric molecules among which the intermolecular interactions of type C—H...Cl and C—H...O are observed (dashed lines in Fig. 1). Intermolecular distances shorter than 0·35 nm which determine the positions of molecules in the crystal structure and contribute to the stability of the crystal lattice are given in Table VI.

To evaluate the planarity of some molecular fragments, to calculate the dihedral angle between pyridazine and phenyl rings and to determine the type of coordination polyhedron around phosphorus atom, the mean planes were lain through four groups of atoms by the least-squares method. The deviations of atoms from these planes and the angles between the mean planes are given in Table VII.

The tetrahedral geometry of the coordination sphere of phosphorus is distorted so that the values of S—P—O angles are higher than those of O—P—O angles (Table V). The interatomic distance P—S(2) 0·1894 nm corresponds to the double bond. As a consequence, the angles O—P—O are lowered under the ideal tetrahedral values and the coordination polyhedron around phosphorus is between trigonal pyramid and tetrahedron. An analogical type of distorted polyhedron was observed by Beckman and Jacobson[16] on the structure of insecticide O,O-dimethyl-O-(3,5,6--trichloro-2-pyridyl)phosphorothionate.

The molecular fragment O(2)—C(3)—C(2)—S(1) is almost parallel with pyridazine ring (dihedral angle 3·4°). The atom C(11) is twisted far from these planes (see Table VII). Bond distances and valence angles in the aliphatic part of the molecule (from C(12) to C(17)) correspond to simple C—C, C—O, C—Cl bonds and to $sp^3$ hybridization of carbon atoms. On the other hand the bond lengths C(4)—N(2), N(2)—N(1), N(1)—C(1), C(1)—O(1), C(3)—C(2), and C(2)—S(1) and the adjacent valence angles (near to 120°) indicate a high delocalization of $\pi$-electrons and a participation of the lone electron pairs of N(1) and S(1) in the conjugation in the pyridazine ring. The geometry of the phenyl ring does not show any significant anomalies in bond lengths C—C and valence angles C—C—C, all being typical for conjugated system.

TABLE I

Basic crystallographic data for fungicide FUNG-P

| | |
|---|---|
| Empirical formula | $C_{17}H_{22}N_2O_4PS_2Cl$ |
| Molecular weight | 448·9 |
| Melting point | 80—82°C |
| Crystallographic system | orthorhombic |
| Space group | *Pccn* |
| Parameters of the unit cell | $a = 1·8719(9)$ nm<br>$b = 3·0426(33)$ nm<br>$c = 0·7616(2)$ nm |
| Volume of the unit cell | $V = 4·3379$ nm$^3$ |
| Number of the formula units in the unit cell | $Z = 8$ |
| Number of electrons in the unit cell | $F(000) = 1\ 872$ |
| Linear absorption coefficient | $\mu = 4·11$ cm$^{-1}$ |
| Characteristic radiation used for the measurement | Cu K$_{\bar{a}}$ = 0·154178 nm |

Because the bond distances C(5)—N(1) 0·1486 nm, C(3)—O(2) 0·1390 nm, P—O(3) 0·1546 nm and P—O(4) 0·1555 nm correspond to simple bonds, the more rigid parts of the molecule can "rotate" around these bonds. The conformation around phosphorus and the mutual rotation between pyridazine and phenyl rings in solid phase are dictated by the energy bariers corresponding to rotations around four bonds mentioned above. These bariers are determined by the forces of surroundings, *i.e.* by intra- and intermolecular interactions given in Table VI.

The most stable conformation of the isolated molecule FUNG-P, *i.e.* without intermolecular interactions, was calculated by optimization of four torsion angles $\varphi$, $\theta$, $\psi$ and $\omega$. The optimal values of these angles for isolated molecule and the corresponding experimental values found in the crystalline state are compared in Table VIII.

TABLE II

Fractional atomic coordinates of hydrogen atoms ($.10^4$) calculated under the assumption of ideal $sp^3$ and $sp^2$ hybridization of carbon atoms

| Atom | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|
| H1 (C4) | 9 436 | 0 002 | 2 131 |
| H2 (C6) | 9 476 | −1 523 | 5 136 |
| H3 (C7) | 9 256 | −2 270 | 4 407 |
| H4 (C8) | 8 287 | −2 455 | 2 535 |
| H5 (C9) | 7 538 | −1 893 | 1 393 |
| H6 (C10) | 7 758 | −1 147 | 2 123 |
| H7 (C11) | 7 818 | 0 019 | 9 978 |
| H8 (C11) | 8 014 | −0 477 | 9 464 |
| H9 (C11) | 7 557 | −0 180 | 8 142 |
| H10 (C12) | 10 172 | 0 751 | 0 237 |
| H11 (C12) | 9 471 | 1 052 | 0 294 |
| H12 (C13) | 10 845 | 1 371 | 1 188 |
| H13 (C13) | 10 497 | 1 436 | 0 714 |
| H14 (C14) | 8 619 | 1 101 | 7 050 |
| H15 (C14) | 8 143 | 1 310 | 5 518 |
| H16 (C15) | 9 116 | 1 770 | 7 581 |
| H17 (C16) | 8 158 | 2 064 | 9 085 |
| H18 (C16) | 7 899 | 1 563 | 9 009 |
| H19 (C16) | 7 792 | 1 876 | 7 340 |
| H20 (C17) | 8 900 | 2 368 | 6 598 |
| H21 (C17) | 8 403 | 2 184 | 5 054 |
| H22 (C17) | 9 232 | 2 056 | 5 118 |

The torsion angle $\varphi$ represents the rotation of the phenyl ring from the plane of pyridazine ring, *i.e.* according to Fig. 1, the torsion angle C(6), C(5), N(1), N(2). The torsion angle $\theta$ corresponds to the rotation of pyridazine ring from the plane P, O(2), C(3) and is defined by atoms P, O(2), C(3), C(4). The remaining torsion angles $\psi$ and $\omega$ defined by atoms O(2), P, O(3), C(12) and O(2), P, O(4), C(14) characterize the geometrical arrangement of atoms in the aliphatic part of the molecule. The experimental value of the torsion angle $\varphi$ is about 35° higher than the value calculated for the isolated molecule. This increase of rotation between the phenyl and pyridazine rings can be attributed to the crystal forces which seem to be highest just in this part

TABLE III

Refined fractional coordinates of non-hydrogen atoms $(.10^4)$. Estimated standard deviations are given in parentheses

| Atom | $x/a$ | $y/b$ | $z/c$ |
| --- | --- | --- | --- |
| Cl | 9 931 (3) | 1 870 (2) | 1 302 (8) |
| S1 | 8 730 (2) | 0 067 (1) | 8 063 (5) |
| S2 | 8 275 (2) | 0 782 (1) | 2 198 (7) |
| P | 9 118 (2) | 0 852 (1) | 3 547 (6) |
| O1 | 8 445 (5) | −0 907 (3) | 6 931 (15) |
| O2 | 9 293 (4) | 0 457 (3) | 4 871 (12) |
| O3 | 9 844 (5) | 0 894 (3) | 2 592 (16) |
| O4 | 9 169 (5) | 1 239 (3) | 4 873 (15) |
| N1 | 8 799 (6) | −0 817 (4) | 4 111 (18) |
| N2 | 9 068 (6) | −0 590 (5) | 2 724 (16) |
| C1 | 8 674 (7) | −0 666 (5) | 5 772 (21) |
| C2 | 8 829 (7) | −0 200 (5) | 6 088 (19) |
| C3 | 9 070 (7) | 0 024 (5) | 4 702 (23) |
| C4 | 9 216 (8) | −0 176 (6) | 3 057 (26) |
| C5 | 8 633 (8) | −1 261 (6) | 3 651 (21) |
| C6 | 9 081 (8) | −1 593 (6) | 4 409 (23) |
| C7 | 8 942 (10) | −2 028 (6) | 3 922 (24) |
| C8 | 8 389 (11) | −2 134 (6) | 2 826 (31) |
| C9 | 7 949 (9) | −1 815 (7) | 2 215 (30) |
| C10 | 8 067 (8) | −1 378 (6) | 2 594 (24) |
| C11 | 7 943 (7) | −0 178 (5) | 9 009 (21) |
| C12 | 9 941 (9) | 1 000 (6) | 0 823 (25) |
| C13 | 10 395 (9) | 1 403 (5) | 0 542 (23) |
| C14 | 8 602 (9) | 1 327 (6) | 6 131 (23) |
| C15 | 8 660 (12) | 1 756 (7) | 6 950 (34) |
| C16 | 8 106 (14) | 1 805 (8) | 8 330 (36) |
| C17 | 8 807 (15) | 2 117 (8) | 5 828 (35) |

Table IV

Bond lengths (nm) in the molecule of FUNG-P. Estimated standard deviation are given in parentheses

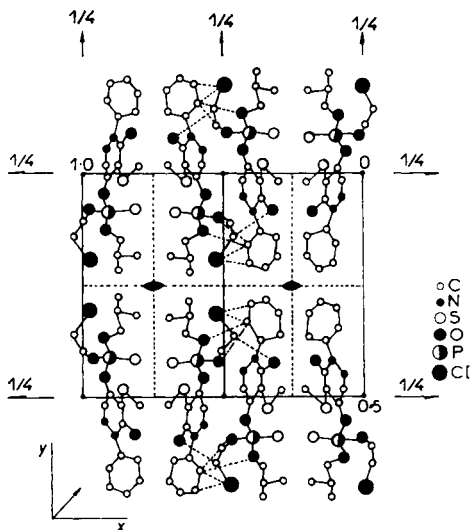| Bond | Bond length | Bond | Bond length |
|------|-------------|------|-------------|
| Cl—C13 | 0·176 (2) | C4—N2 | 0·141 (2) |
| C13—C12 | 0·151 (2) | N1—N2 | 0·136 (1) |
| C12—O3 | 0·140 (2) | N1—C1 | 0·137 (1) |
| P—C2 | 0·160 (1) | N1—C5 | 0·149 (2) |
| P—O2 | 0·155 (1) | C1—O1 | 0·122 (1) |
| P—O4 | 0·155 (1) | C1—C2 | 0·147 (2) |
| P—S2 | 0·189 (1) | S1—C2 | 0·172 (1) |
| C14—O4 | 0·145 (1) | S1—C11 | 0·180 (1) |
| C14—C15 | 0·145 (2) | C5—C6 | 0·139 (2) |
| C15—C16 | 0·148 (2) | C6—C7 | 0·140 (2) |
| C15—C17 | 0·142 (2) | C7—C8 | 0·137 (2) |
| C3—O2 | 0·139 (1) | C8—C9 | 0·135 (2) |
| C3—C2 | 0·133 (2) | C9—C10 | 0·138 (2) |
| C3—C4 | 0·142 (2) | C10—C5 | 0·136 (2) |



FIG. 1

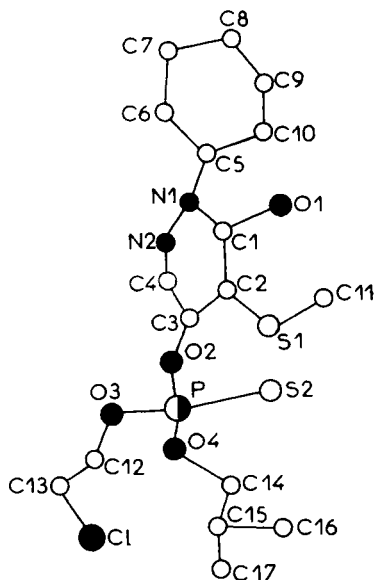Projection of the crystal structure of thio-phosphate fungicide FUNG-P along the *c* axes

FIG. 2

Numbering of atoms in the molecule of thio-phosphate fungicide FUNG-P

of the molecule (some interactions are shown in Fig. 1 by dashed lines). The values of other torsion angles $\theta$, $\psi$, and $\omega$ are near to those calculated for the isolated molecule. It shows that the structure in the crystalline phase is very near to the relaxed structure, *i.e.* the intermolecular forces in the crystal does not cause important changes with respect to the structure of the isolated molecule.

TABLE V

Valence angles (deg) in the molecule of fungicide FUNG-P. Estimated standard deviations are given in parentheses

| Atoms | Angle | Atoms | Angle |
|-------|-------|-------|-------|
| Cl—C13—C12 | 109 (1) | C1—C2—C3 | 115 (1) |
| C13—C12—O3 | 113 (1) | C1—C2—S1 | 125 (1) |
| C12—O3—P | 126 (1) | C3—C2—S1 | 119 (1) |
| O2—P—O3 | 100 (1) | N1—H2—C4 | 114 (1) |
| O2—P—O4 | 98 (1) | C2—S1—C11 | 104 (1) |
| O2—P—S2 | 115 (0·4) | O1—C1—C2 | 122 (1) |
| O3—P—O4 | 101 (1) | O1—C1—N1 | 122 (1) |
| O3—P—S2 | 119 (1) | N1—C1—C2 | 116 (1) |
| O4—P—S2 | 119 (0·4) | C1—N1—N2 | 128 (1) |
| P—O4—C14 | 121 (1) | C1—N1—C5 | 120 (1) |
| O4—C14—C15 | 113 (1) | N2—N1—C5 | 112 (1) |
| C14—C15—C16 | 110 (2) | N1—C5—C6 | 115 (1) |
| C14—C15—C17 | 117 (2) | N1—C5—C10 | 121 (1) |
| C16—C15—C17 | 119 (2) | C6—C5—C10 | 124 (1) |
| P—O2—C3 | 126 (1) | C5—C6—C7 | 115 (1) |
| O2—C3—C4 | 116 (2) | C6—C7—C8 | 121 (1) |
| O2—C3—C2 | 121 (1) | C7—C8—C9 | 120 (2) |
| C2—C3—C4 | 123 (1) | C8—C9—C10 | 121 (2) |
| C3—C4—N2 | 123 (2) | C5—C10—C9 | 117 (2) |

TABLE VI

Intra- and intermolecular contacts $<0\cdot35$ nm of van der Waals type

| | | | |
|-------|--------|-------|--------|
| H6 ... C1 | 0·3115 | H6 ... O4[a] | 0·2680 |
| H7 ... C1 | 0·3075 | H17 ... C1[a] | 0·3025 |
| H13 ... O1[a] | 0·2412 | H10 ... O1[a] | 0·2373 |
| H6 ... O3[a] | 0·2877 | | |

[a] Symmetry equivalent position $-x$, $-y$, $-z$.

The calculation of the electron structure provided several indices which characterize the distribution of electron density in the molecule and the multiplicity of bonds. The net charges on the individual atoms and the values of Wiberg indices for the conformation of molecule FUNG-P with angles $\varphi = -35°$, $\theta = 50°$, $\psi = -60°$ and $\omega = 60°$ are given in Table IX. The net charges give a picture of distribution of electron density in the molecule and the Wiberg indices characterize the multipli-

TABLE VII

a) Coefficients of the mean planes $Ax + By + Cz = D$ through the selected atoms ($.10^4$)

| Plane | Atoms defining the plane | A | B | C | D |
|-------|--------------------------|---|---|---|---|
| (1) | C5, C6, C7, C8, C9, C10 | 5 000 | 870 | −7 953 | 71 238 |
| (2) | C1, C2, C3, C4, N1, N2 | −9 305 | 2 383 | −2 781 | 8 036 |
| (3) | P, O2, O3, O4 | −8 355 | −862 | −5 428 | 4 987 |
| (4) | O2, C3, C2, S1 | −9 237 | 2 902 | −2 502 | 5 810 |

b) Deviations of some atoms from the mean planes ($.10^4$), nm

| Atoms | (1) | Atoms | (2) | Atoms | (3) | (4) |
|-------|-----|-------|-----|-------|-----|-----|
| C5 | 20 | C1 | −10 | P1 | 549 | 891 |
| C6 | −18 | C2 | −9 | O2 | −167 | −11 |
| C7 | 0 | C3 | 26 | O3 | −202 | — |
| C8 | 19 | C4 | −24 | O4 | −179 | — |
| C9 | −19 | N1 | 14 | S2 | 2 443 | — |
| C10 | 0 | N2 | 3 | S1 | — | 9 |
| N1 | 50 | O1 | −31 | C2 | — | −21 |
| O1 | −2 078 | O2 | −83 | C3 | — | 23 |
| | | S1 | −61 | C11 | — | 973 |
| | | C11 | 930 | C12 | 175 | |

c) Dihedral angles between the mean planes, deg

| Plane | Angle | Plane | Angle |
|-------|-------|-------|-------|
| (1)—(2) | 108·4 | (2)—(3) | 24·8 |
| (1)—(3) | 94·4 | (2)—(4) | 3·4 |
| (1)—(4) | 109·3 | (3)—(4) | 28·1 |

city of bonds. The most negative net charges are at S(2) and O(1). The most positive charges are at P, C(1), C(12) and C(3). The bonds P—O and C—N in the pyridazine ring are strongly polarized.

TABLE VIII

Experimental and calculated values of torsion angles (deg) in the molecule of FUNG-P. Estimated standard deviations are given in parentheses

| Atoms | Torsion angle | Experimental value | Calculated value |
|---|---|---|---|
| C6, C5, N1, N2 | $\varphi$ | −70 (2) | −35 |
| P, O2, C3, C4 | $\theta$ | 52 (1) | 50 |
| O2, P, O3, C12 | $\psi$ | −35 (1) | −60 |
| O2, P, O4, C14 | $\omega$ | 76 (1) | 60 |

TABLE IX

Net charges on the individual atoms and Wiberg indices $I_w$ for fungicide FUNG-P

| Atom | Net charge $Q$ | Bond | $I_w$ |
|---|---|---|---|
| N1 | −0·17 | C1—N1 | 1·48 |
| N2 | −0·12 | C1—O1 | 1·63 |
| C1 | 0·24 | C1—C2 | 1·26 |
| O1 | −0·28 | C2—S1 | 1·29 |
| C2 | 0·18 | C2—C3 | 1·51 |
| C3 | 0·22 | N1—N2 | 1·59 |
| C4 | 0·05 | N1—C5 | 1·08 |
| S1 | −0·19 | N2—C4 | 1·62 |
| C11 | 0·11 | C3—C4 | 1·40 |
| O2 | −0·13 | C3—O2 | 0·94 |
| P | 0·23 | P—O2 | 1·39 |
| S2 | −0·31 | P—O3 | 1·33 |
| O3 | −0·19 | P—O4 | 1·41 |
| O4 | −0·18 | P—S2 | 2·09 |
| C12 | 0·22 | O3—C12 | 0·93 |
| C13 | 0·06 | C12—C13 | 0·94 |
| Cl | −0·12 | C13—Cl | 1·28 |
| C14—C17 | −0·03 − 0·04 | O4—C14 | 1·02 |
| C5 | 0·10 | C5 up C10 | 1·46 |
| C6—C10 | −0·04 − 0·06 | C14 up C17 | 0·95 |
| | | S1—C11 | 1·24 |

The values of Wiberg indices enable to estimate the multiplicity of individual bonds. The highest value was obtained for P—S(2) bond. The bonds C(1)—O(1), N(2)—C(4), N(1)—N(2), C(2)—C(3) and also the bonds of the phenyl ring have character of the partial double or conjugated bond. The Wiberg indices for the bonds N(1)—C(5), $I_w = 1.08$ and C(3)—O(2), $I_w = 0.96$ clearly indicate single bonds. A conjugation between the phenyl and pyridazine rings is suppressed by the mutual rotation of the two rings (35° for isolated molecule and 70.3° in the crystal). These results of CNDO/2 calculations are in a good agreement with the experimental values of bond lengths found by X-ray structure analysis (Table IV).

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