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(*R*,*S*)-Diethyl {[5-(2,4-dichlorophenyl)-1,3,4-thiadiazol-2-ylamino](phenyl)-methyl}phosphonate

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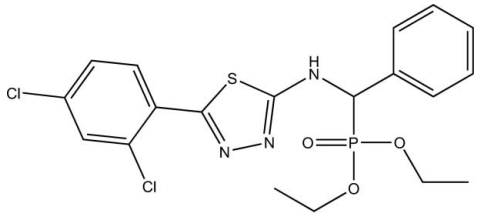
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.009 Å; R factor = 0.085; wR factor = 0.154; data-to-parameter ratio = 17.2.

In the molecule of the title compound, $C_{19}H_{20}Cl_2N_3O_3PS$, intramolecular C—H···N hydrogen bonding results in the formation of a nearly planar five-membered ring. In the crystal structure, intermolecular N—H···O and C—H···N hydrogen bonds link the molecules.

Related literature

For related literature, see: Nakagawa *et al.* (1996); Wang *et al.* (1999). For bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

$C_{19}H_{20}Cl_2N_3O_3PS$
M_r = 472.31
Monoclinic, $P2_1/n$
a = 8.4870 (17) Å
b = 16.530 (3) Å
c = 15.703 (3) Å
β = 94.47 (3)°
V = 2196.3 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.49 mm^{-1}
T = 298 (2) K
0.40 × 0.10 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.828, T_{max} = 0.953
4609 measured reflections
4312 independent reflections
3145 reflections with $I > 2\sigma(I)$
R_{int} = 0.052
3 standard reflections
every 200 reflections
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.085
$wR(F^2)$ = 0.154
S = 1.17
4312 reflections
250 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.70 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O2^{i}	0.86	2.09	2.815 (7)	141
C4—H4A···N3^{ii}	0.97	2.56	3.321 (11)	134
C15—H15A···N3	0.93	2.45	2.783 (7)	101

Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $x-\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Siemens, 1996); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HK2370).

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supplementary materials

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(*R*,*S*)-Diethyl {[5-(2,4-dichlorophenyl)-1,3,4-thiadiazol-2-ylamino](phenyl)methyl}phosphonate

L.-H. Yin, R. Wan, W.-Y. Wu, B. Wang and J.-T. Wang

Comment

1,3,4-Thiadiazole derivatives represent an interesting class of compounds possessing broad spectrum biological activities (Nakagawa *et al.*, 1996; Wang *et al.*, 1999). These compounds are known to exhibit diverse biological effects, such as insecticidal and fungicidal activities (Wang *et al.*, 1999).

In the molecule of (I) (Fig. 1), the bond lengths and angles are within normal ranges (Allen *et al.*, 1987). Rings A (C6—C11), B (S/N2/N3/C12/C13) and C (C14—C19) are, of course, planar and the dihedral angles between them are A/B = 74.19 (3)°, A/C = 75.91 (3)° and B/C = 10.69 (3)°. The intramolecular C—H···N hydrogen bond (Table 1) results in the formation of a nearly planar five-membered ring; D (N3/C13—C15/H7A), which is oriented with respect to the adjacent rings B and C, at dihedral angles of B/D = 10.93 (2)° and C/D = 5.632 (3)°.

In the crystal structure, intermolecular N—H···O and C—H···N hydrogen bonds (Table 1, Fig. 2)) link the molecules, in which they seem to be effective in the stabilization of the structure.

Experimental

For the preparation of the title compound, *N*-benzylidene-5-(2,4-dichlorophenyl) −1,3,4-thiadiazol-2-amine (2 mmol) and diethyl phosphite (5 mmol) were added in a flask (25 ml) and reacted in an oil bath (363 K) for 6 h. After cooling and filtering, crude compound (I) was obtained, and recrystallized from ethanol. Crystals of (I) suitable for X-ray analysis were obtained by slow evaporation of an acetone solution.

Refinement

H atoms were positioned geometrically, with N—H = 0.86 Å (for NH) and C—H = 0.98, 0.97 and 0.96 Å for methine, methylene and methyl H atoms, respectively, and constrained to ride on their parent atoms, with $U_{iso}(H) = xU_{eq}(C,N)$, where x = 1.5 for methyl H and x = 1.2 for all other H atoms.

Figures

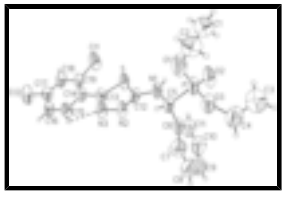

Fig. 1. The molecular structure of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines.

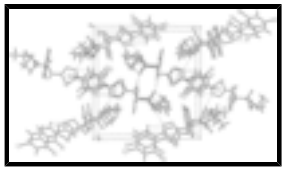

Fig. 2. A packing diagram of (I). Hydrogen bonds are shown as dashed lines.

(*R*,*S*)-Diethyl {[5-(2,4-dichlorophenyl)-1,3,4-thiadiazol-2-ylamino](phenyl)methyl}phosphonate

Crystal data

$C_{19}H_{20}Cl_2N_3O_3PS$	F_{000} = 976
M_r = 472.31	D_x = 1.428 Mg m^{-3}
Monoclinic, $P2_1/n$	Melting point: 453-454 K
Hall symbol: -P 2yn	Mo $K\alpha$ radiation λ = 0.71073 Å
a = 8.4870 (17) Å	Cell parameters from 25 reflections
b = 16.530 (3) Å	θ = 10–12º
c = 15.703 (3) Å	μ = 0.49 mm^{-1}
β = 94.47 (3)º	T = 298 (2) K
V = 2196.3 (7) Å^3	Needle, colorless
Z = 4	0.40 × 0.10 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer	R_{int} = 0.052
Radiation source: fine-focus sealed tube	θ_{max} = 26.0º
Monochromator: graphite	θ_{min} = 1.8º
T = 298(2) K	h = −10→10
ω/2θ scans	k = 0→20
Absorption correction: ψ scan (North *et al.*, 1968)	l = 0→19
T_{min} = 0.828, T_{max} = 0.953	3 standard reflections
4609 measured reflections	every 200 reflections
4312 independent reflections	intensity decay: none
3145 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.085	H-atom parameters constrained
$wR(F^2)$ = 0.154	$w = 1/[\sigma^2(F_o^2) + (0.1265P)^2 + 1.3578P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.17	$(\Delta/\sigma)_{max} < 0.001$
4312 reflections	$\Delta\rho_{max}$ = 0.31 e Å^{-3}

250 parameters	$\Delta\rho_{min} = -0.70$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.3460 (3)	0.37335 (12)	0.14352 (10)	0.1114 (7)
Cl2	0.3666 (2)	0.44309 (12)	−0.18670 (9)	0.1133 (8)
S	0.1558 (2)	0.48605 (11)	0.25006 (9)	0.0806 (6)
P	0.0393 (2)	0.65490 (13)	0.52266 (9)	0.0760 (6)
O1	0.2180 (6)	0.6788 (3)	0.5237 (2)	0.1143 (17)
O2	0.0005 (6)	0.5841 (3)	0.5707 (2)	0.1010 (16)
O3	−0.0427 (5)	0.7339 (3)	0.5529 (2)	0.0810 (13)
N1	0.0476 (5)	0.5763 (3)	0.3769 (2)	0.0743 (15)
H1A	0.0697	0.5357	0.4099	0.089*
N2	0.0586 (6)	0.6318 (3)	0.2402 (3)	0.0777 (15)
N3	0.1044 (6)	0.6122 (3)	0.1607 (3)	0.0800 (16)
C1	0.3610 (7)	0.6550 (4)	0.6493 (4)	0.100
H1B	0.4266	0.6728	0.6983	0.150*
H1C	0.4184	0.6170	0.6174	0.150*
H1D	0.2679	0.6294	0.6678	0.150*
C2	0.3175 (8)	0.7211 (4)	0.5980 (4)	0.104
H2C	0.4090	0.7483	0.5780	0.125*
H2D	0.2548	0.7596	0.6275	0.125*
C3	−0.1313 (9)	0.7382 (5)	0.6870 (5)	0.139 (3)
H3B	−0.2156	0.7363	0.7243	0.209*
H3C	−0.0786	0.7895	0.6929	0.209*
H3D	−0.0574	0.6956	0.7017	0.209*
C4	−0.1941 (9)	0.7282 (5)	0.6014 (4)	0.126 (3)
H4A	−0.2685	0.7708	0.5842	0.151*
H4B	−0.2454	0.6760	0.5928	0.151*
C5	−0.0214 (6)	0.6487 (4)	0.4094 (3)	0.0625 (16)
H5A	0.0225	0.6954	0.3810	0.075*
C6	−0.1952 (8)	0.6534 (5)	0.3975 (3)	0.0728 (17)
C7	−0.2645 (8)	0.7291 (5)	0.3791 (4)	0.094 (2)
H7A	−0.2045	0.7752	0.3711	0.112*

C8	−0.4350 (10)	0.7307 (6)	0.3735 (4)	0.114 (3)
H8A	−0.4841	0.7805	0.3632	0.137*
C9	−0.5298 (10)	0.6650 (6)	0.3820 (4)	0.107 (2)
H9A	−0.6394	0.6689	0.3761	0.128*
C10	−0.4547 (10)	0.5930 (5)	0.3999 (4)	0.105 (2)
H10A	−0.5146	0.5470	0.4085	0.126*
C11	−0.2943 (8)	0.5873 (5)	0.4053 (4)	0.091 (2)
H11A	−0.2487	0.5366	0.4147	0.109*
C12	0.0776 (6)	0.5735 (4)	0.2916 (3)	0.0647 (16)
C13	0.1598 (7)	0.5399 (4)	0.1552 (3)	0.0660 (17)
C14	0.2134 (6)	0.5107 (4)	0.0727 (3)	0.0646 (16)
C15	0.1763 (7)	0.5587 (4)	0.0007 (3)	0.0771 (18)
H15A	0.1172	0.6056	0.0058	0.092*
C16	0.2262 (7)	0.5374 (4)	−0.0786 (3)	0.0709 (17)
H16A	0.2031	0.5702	−0.1261	0.085*
C17	0.3105 (7)	0.4667 (4)	−0.0856 (3)	0.0694 (17)
C18	0.3452 (7)	0.4183 (4)	−0.0185 (3)	0.0785 (19)
H18A	0.4053	0.3718	−0.0239	0.094*
C19	0.2892 (7)	0.4390 (4)	0.0592 (3)	0.0715 (18)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.180 (2)	0.0953 (15)	0.0658 (11)	0.0132 (14)	0.0529 (11)	−0.0004 (10)
Cl2	0.1685 (18)	0.1257 (18)	0.0526 (9)	−0.0267 (15)	0.0524 (10)	−0.0308 (10)
S	0.1088 (13)	0.0911 (14)	0.0463 (8)	−0.0013 (11)	0.0348 (8)	−0.0076 (9)
P	0.0906 (14)	0.0975 (16)	0.0420 (9)	−0.0043 (12)	0.0253 (8)	−0.0148 (10)
O1	0.119 (4)	0.125 (5)	0.061 (3)	−0.016 (4)	0.025 (2)	−0.030 (3)
O2	0.168 (5)	0.085 (4)	0.056 (2)	0.003 (3)	0.043 (3)	−0.002 (2)
O3	0.094 (3)	0.086 (4)	0.056 (2)	0.043 (3)	−0.043 (2)	−0.006 (2)
N1	0.096 (4)	0.093 (4)	0.038 (2)	0.009 (3)	0.028 (2)	−0.005 (3)
N2	0.101 (4)	0.087 (4)	0.051 (3)	−0.009 (3)	0.039 (3)	0.000 (3)
N3	0.115 (4)	0.080 (4)	0.050 (3)	−0.004 (3)	0.039 (3)	−0.009 (3)
C1	0.100 (4)	0.107 (3)	0.100 (3)	−0.001 (2)	0.008 (2)	0.000 (3)
C2	0.104 (4)	0.108 (4)	0.104 (4)	−0.002 (2)	0.007 (3)	0.000 (3)
C3	0.149 (6)	0.151 (7)	0.118 (5)	0.009 (6)	0.015 (5)	−0.007 (5)
C4	0.156 (6)	0.129 (6)	0.099 (5)	0.037 (5)	0.040 (4)	−0.006 (5)
C5	0.065 (4)	0.076 (4)	0.050 (3)	−0.001 (3)	0.028 (3)	−0.009 (3)
C6	0.081 (4)	0.097 (5)	0.042 (3)	−0.004 (4)	0.018 (3)	−0.012 (3)
C7	0.090 (4)	0.112 (5)	0.080 (4)	0.009 (4)	0.013 (4)	−0.008 (4)
C8	0.109 (5)	0.130 (6)	0.104 (5)	0.019 (5)	0.014 (5)	−0.015 (5)
C9	0.105 (5)	0.144 (6)	0.074 (4)	−0.005 (4)	0.022 (4)	−0.005 (5)
C10	0.104 (5)	0.134 (6)	0.079 (4)	−0.025 (5)	0.029 (4)	−0.010 (5)
C11	0.096 (4)	0.112 (5)	0.069 (4)	−0.018 (4)	0.032 (4)	−0.015 (4)
C12	0.061 (4)	0.084 (4)	0.052 (3)	−0.003 (3)	0.027 (3)	−0.019 (3)
C13	0.075 (4)	0.081 (4)	0.043 (3)	−0.010 (4)	0.020 (3)	−0.005 (3)
C14	0.066 (4)	0.084 (4)	0.046 (3)	−0.022 (3)	0.017 (3)	−0.007 (3)
C15	0.100 (4)	0.088 (5)	0.045 (3)	0.000 (4)	0.019 (3)	−0.003 (3)

C16	0.085 (4)	0.091 (5)	0.038 (3)	−0.019 (4)	0.014 (3)	−0.008 (3)
C17	0.089 (4)	0.075 (5)	0.047 (3)	−0.021 (4)	0.016 (3)	−0.016 (3)
C18	0.096 (4)	0.090 (5)	0.053 (3)	−0.014 (4)	0.030 (3)	−0.018 (3)
C19	0.087 (4)	0.082 (4)	0.050 (3)	−0.012 (4)	0.031 (3)	−0.003 (3)

Geometric parameters (Å, °)

Cl1—C19	1.751 (6)	C4—H4A	0.9700
Cl2—C17	1.737 (5)	C4—H4B	0.9700
S—C13	1.737 (6)	C5—C6	1.475 (7)
S—C12	1.738 (6)	C5—H5A	0.9800
P—O2	1.444 (4)	C6—C11	1.391 (8)
P—O1	1.567 (5)	C6—C7	1.402 (9)
P—O3	1.570 (4)	C7—C8	1.443 (9)
P—C5	1.815 (5)	C7—H7A	0.9300
O1—C2	1.552 (7)	C8—C9	1.365 (10)
O3—C4	1.547 (7)	C8—H8A	0.9300
N1—C12	1.383 (6)	C9—C10	1.368 (10)
N1—C5	1.443 (6)	C9—H9A	0.9300
N1—H1A	0.8600	C10—C11	1.361 (9)
N2—C12	1.260 (7)	C10—H10A	0.9300
N2—N3	1.376 (5)	C11—H11A	0.9300
N3—C13	1.289 (7)	C13—C14	1.487 (6)
C1—C2	1.391 (7)	C14—C19	1.372 (8)
C1—H1B	0.9600	C14—C15	1.397 (7)
C1—H1C	0.9600	C15—C16	1.392 (7)
C1—H1D	0.9600	C15—H15A	0.9300
C2—H2C	0.9700	C16—C17	1.379 (8)
C2—H2D	0.9700	C16—H16A	0.9300
C3—C4	1.416 (8)	C17—C18	1.338 (8)
C3—H3B	0.9600	C18—C19	1.387 (7)
C3—H3C	0.9600	C18—H18A	0.9300
C3—H3D	0.9600		
C13—S—C12	86.0 (3)	P—C5—H5A	108.2
O2—P—O1	117.3 (3)	C11—C6—C7	118.2 (7)
O2—P—O3	113.1 (2)	C11—C6—C5	123.5 (7)
O1—P—O3	103.8 (3)	C7—C6—C5	118.2 (7)
O2—P—C5	114.0 (3)	C6—C7—C8	115.6 (8)
O1—P—C5	103.0 (2)	C6—C7—H7A	122.2
O3—P—C5	104.2 (3)	C8—C7—H7A	122.2
C2—O1—P	126.2 (4)	C9—C8—C7	125.1 (9)
C4—O3—P	120.2 (4)	C9—C8—H8A	117.4
C12—N1—C5	118.8 (5)	C7—C8—H8A	117.4
C12—N1—H1A	120.6	C8—C9—C10	116.3 (8)
C5—N1—H1A	120.6	C8—C9—H9A	121.8
C12—N2—N3	111.7 (5)	C10—C9—H9A	121.8
C13—N3—N2	114.1 (5)	C11—C10—C9	121.4 (8)
C2—C1—H1B	109.5	C11—C10—H10A	119.3
C2—C1—H1C	109.5	C9—C10—H10A	119.3

H1B—C1—H1C	109.5	C10—C11—C6	123.2 (8)
C2—C1—H1D	109.5	C10—C11—H11A	118.4
H1B—C1—H1D	109.5	C6—C11—H11A	118.4
H1C—C1—H1D	109.5	N2—C12—N1	124.8 (6)
C1—C2—O1	100.7 (6)	N2—C12—S	115.4 (4)
C1—C2—H2C	111.6	N1—C12—S	119.7 (5)
O1—C2—H2C	111.6	N3—C13—C14	119.7 (5)
C1—C2—H2D	111.6	N3—C13—S	112.7 (4)
O1—C2—H2D	111.6	C14—C13—S	127.5 (5)
H2C—C2—H2D	109.4	C19—C14—C15	116.3 (5)
C4—C3—H3B	109.5	C19—C14—C13	126.4 (6)
C4—C3—H3C	109.5	C15—C14—C13	117.2 (6)
H3B—C3—H3C	109.5	C16—C15—C14	121.0 (6)
C4—C3—H3D	109.5	C16—C15—H15A	119.5
H3B—C3—H3D	109.5	C14—C15—H15A	119.5
H3C—C3—H3D	109.5	C17—C16—C15	118.8 (6)
C3—C4—O3	101.2 (6)	C17—C16—H16A	120.6
C3—C4—H4A	111.5	C15—C16—H16A	120.6
O3—C4—H4A	111.5	C18—C17—C16	121.9 (6)
C3—C4—H4B	111.5	C18—C17—Cl2	121.7 (6)
O3—C4—H4B	111.5	C16—C17—Cl2	116.4 (5)
H4A—C4—H4B	109.3	C17—C18—C19	118.4 (6)
N1—C5—C6	115.4 (5)	C17—C18—H18A	120.8
N1—C5—P	107.6 (4)	C19—C18—H18A	120.8
C6—C5—P	109.0 (3)	C14—C19—C18	123.2 (6)
N1—C5—H5A	108.2	C14—C19—Cl1	121.5 (4)
C6—C5—H5A	108.2	C18—C19—Cl1	114.8 (5)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1A···O2^{i}	0.86	2.09	2.815 (7)	141
C4—H4A···N3^{ii}	0.97	2.56	3.321 (11)	134
C15—H15A···N3	0.93	2.45	2.783 (7)	101

Symmetry codes: (i) −*x*, −*y*+1, −*z*+1; (ii) *x*−1/2, −*y*+3/2, *z*+1/2.

Fig. 1

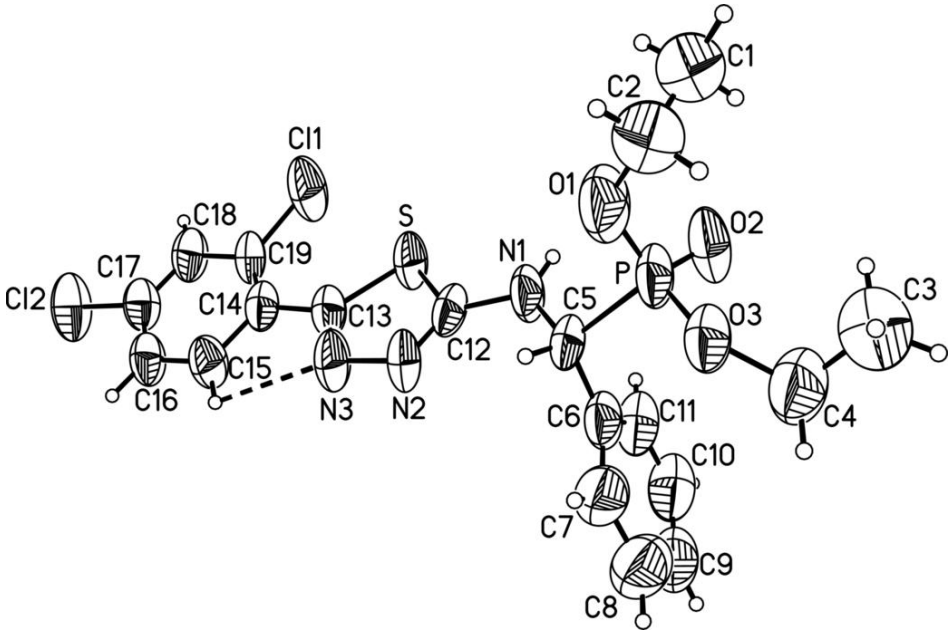
C1
C2
Cl1
O1
C18
S
O2
N1
C17
C19
P
C3
Cl2
C14
C13
C5
O3
C12
C15
C16
N3
N2
C6
C11
C4
C10
C7
C9
C8

Fig. 2