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3-Chloro-1,1,1-trifluoro-3-(triphenylphosphoranylidene)propan-2-one

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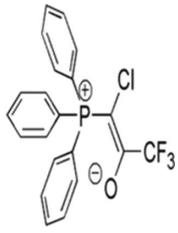
Key indicators: single-crystal X-ray study; T = 273 K; mean σ(C–C) = 0.003 Å; R factor = 0.035; wR factor = 0.090; data-to-parameter ratio = 13.8.

The title compound, $C_{21}H_{15}ClF_3OP$, was obtained by a convenient and efficient one-pot synthesis. The length of the C=C bond indicates a large enolic contribution to the structure. Intra- and intermolecular C—H···O hydrogen bonds are present in the crystal structure.

Related literature

For general background, see: Goldman (1969); Iseki (1998); Ge *et al.* (2007). For bond-length data, see: Allen *et al.* (1987). For related literature, see: Berclaz *et al.* (1999).



Experimental

Crystal data

$C_{21}H_{15}ClF_3OP$
M_r = 406.75
Monoclinic, $P2_1/c$
a = 10.6377 (9) Å
b = 9.8603 (9) Å
c = 18.3754 (16) Å
β = 96.0590 (10)°
V = 1916.6 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.32 mm^{-1}
T = 273 (2) K
0.30 × 0.30 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.911, T_{max} = 0.939
9644 measured reflections
3391 independent reflections
3014 reflections with $I > 2\sigma(I)$
R_{int} = 0.015

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.090
S = 1.03
3391 reflections
245 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.33 e Å^{-3}

Table 1
Selected bond length (Å).

C19—C20	1.384 (3)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2···O1	0.93	2.50	3.1460	127
C17—H17···O1^{i}	0.93	2.49	3.1937	133

Symmetry code: (i) $x, y+1, z$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); 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: HK2266).

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supplementary materials

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3-Chloro-1,1,1-trifluoro-3-(triphenylphosphoranylidene)propan-2-one

Z.-X. Wang, H.-Z. Jiang, W. Wan, F.-L. Ge and J. Hao

Comment

Fluorine-containing compounds have received considerable attention because of their pharmaceutical applications and unique physical properties (Goldman, 1969; Iseki, 1998). As one part of our ongoing studies on the synthesis of organofluorine compounds, we focused our attention on the synthesis of fluorinated imidoyl chloride intermediates (Ge *et al.*, 2007). The phosphonium ylide of (3) was obtained unexpectedly, while searching of a novel flourine-containing benzimidazole.

In the molecule of the title compound, (3), (Fig. 1), the bond lengths and angles are generally within normal ranges (Allen *et al.*, 1987), where the bonds P1—C19 [1.7509 (17) Å] and C20—O1 [1.244 (2) Å] are longer than the commonly corresponding double bonds P=C [1.66 Å] in $Ph_3P{=}CH_2$ and C=O [1.22 Å] in $(CH_3)_2CO$. In addition, the bonds C19—C20 [1.384 (3) Å] and C19—Cl1 [1.734 (18) Å] are shorter than the common C—C and C—Cl [1.77 Å] single bonds. Furthermore, the bond angles C20—C19—Cl1 [124.21 (14)°] and O1—C20—C19 [123.49 (17)°] are close to those of double bonds. These results strongly indicate that C19—C20 bond has significantly double bond character in the enolic structure of phosphonium ylides (3) (Berclaz *et al.*, 1999), which could be stabilized by the strong electron-withdrawing of the trifluoro- methyl group.

Rings A (C1—C6), B (C7—C12) and C (C13—C18) are, of course, planar and the dihedral angles between them are A/B = 75.23 (2)°, A/C = 69.69 (3)° and B/C = 72.37 (3)°.

In the crystal structure, intra- and intermolecular C—H···O hydrogen bonds (Table 1, Fig. 1), linking the molecules, seem to be effective in the stabilization of the structure.

Experimental

For the preparation of the title compound, Ph_3P (34.5 g, 132 mmol), NEt_3 (18.2 ml, 132 mmol), CCl_4 (21.1 ml, 220 mmol) and TFA (3.4 ml, 44 mmol) was added to a 200 ml three-necked round bottom flask equipped with condenser and magnetic stir bar at 273 K under nitrogen atmosphere and stirred for 10 min. Subsequently, the reaction mixture was allowed to reflux for 3 h. After cooling, the solvent was removed by rotary evaporator and the residue was washed carefully with the solution of petroleum ether and ethyl acetate (2:1) for three times, the precipitate was removed *via* filtration. The filtrate was combined and concentrated by rotary evaporator. The residue was then purified by column chromatography to offer the product (yield; 59%).

Refinement

H atoms were positioned geometrically, with C—H = 0.93 Å for aromatic H atoms, and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$.

Figures

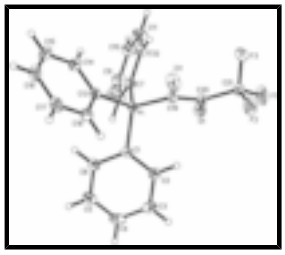

Fig. 1. The molecular structure of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

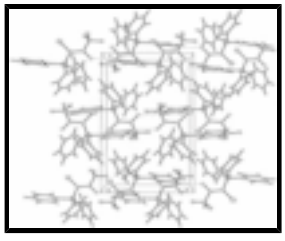

Fig. 2. A packing diagram for (3). Hydrogen bonds are shown as dashed lines.

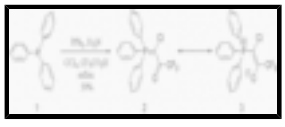

Fig. 3. The reaction scheme for the formation of (3).

3-Chloro-1,1,1-trifluoro-3-(triphenylphosphoranylidene)propan-2-one

Crystal data

$C_{21}H_{15}ClF_3OP$	F_{000} = 832
M_r = 406.75	D_x = 1.410 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 5734 reflections
a = 10.6377 (9) Å	θ = 2.3–27.4º
b = 9.8603 (9) Å	μ = 0.32 mm^{-1}
c = 18.3754 (16) Å	T = 273 (2) K
β = 96.0590 (10)º	Block, colorless
V = 1916.6 (3) Å^3	0.30 × 0.30 × 0.20 mm
Z = 4	

Data collection

Bruker SMART CCD area-detector diffractometer	3014 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	R_{int} = 0.015
Monochromator: graphite	θ_{max} = 25.1º
T = 273(2) K	θ_{min} = 2.2º
φ and ω scans	h = −12→12
Absorption correction: none	k = −11→11
9644 measured reflections	l = −18→21
3391 independent reflections	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.035$	$w = 1/[\sigma^2(F_o^2) + (0.0388P)^2 + 0.9546P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.090$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.03$	$\Delta\rho_{max} = 0.34$ e Å^{-3}
3391 reflections	$\Delta\rho_{min} = -0.33$ e Å^{-3}
245 parameters	Extinction correction: SHELXL97, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0079 (7)
Secondary atom site location: difference Fourier map	

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	0.78417 (7)	0.43490 (6)	−0.06671 (3)	0.0659 (2)
P1	0.78933 (4)	0.37901 (4)	0.09492 (2)	0.03432 (14)
F1	0.84707 (18)	−0.00956 (15)	−0.07485 (9)	0.0985 (6)
F2	0.90527 (15)	0.17805 (19)	−0.11684 (8)	0.0966 (6)
F3	0.71153 (13)	0.13165 (16)	−0.11872 (8)	0.0822 (5)
O1	0.83346 (15)	0.10340 (14)	0.05088 (8)	0.0577 (4)
C1	0.93696 (16)	0.37741 (17)	0.15278 (9)	0.0378 (4)
C2	1.03455 (18)	0.2950 (2)	0.13624 (11)	0.0493 (5)
H2	1.0245	0.2395	0.0951	0.059*
C3	1.1475 (2)	0.2951 (3)	0.18098 (14)	0.0652 (6)
H3	1.2134	0.2395	0.1698	0.078*
C4	1.1630 (2)	0.3765 (3)	0.24157 (13)	0.0670 (7)
H4	1.2394	0.3760	0.2713	0.080*
C5	1.0667 (2)	0.4587 (3)	0.25870 (12)	0.0654 (6)
H5	1.0775	0.5133	0.3002	0.078*
C6	0.95318 (19)	0.4606 (2)	0.21433 (11)	0.0539 (5)

H6	0.8880	0.5172	0.2256	0.065*
C7	0.67461 (16)	0.27865 (18)	0.13649 (10)	0.0394 (4)
C8	0.69440 (19)	0.2353 (2)	0.20828 (11)	0.0517 (5)
H8	0.7684	0.2585	0.2371	0.062*
C9	0.6036 (2)	0.1573 (3)	0.23702 (12)	0.0670 (6)
H9	0.6169	0.1283	0.2854	0.080*
C10	0.4946 (2)	0.1222 (3)	0.19517 (14)	0.0703 (7)
H10	0.4340	0.0699	0.2151	0.084*
C11	0.4747 (2)	0.1643 (3)	0.12389 (14)	0.0703 (7)
H11	0.4007	0.1401	0.0953	0.084*
C12	0.56394 (19)	0.2424 (2)	0.09450 (12)	0.0570 (5)
H12	0.5498	0.2710	0.0461	0.068*
C13	0.73744 (17)	0.55267 (18)	0.09040 (10)	0.0399 (4)
C14	0.6163 (2)	0.5899 (2)	0.10284 (11)	0.0531 (5)
H14	0.5590	0.5247	0.1152	0.064*
C15	0.5808 (2)	0.7252 (3)	0.09677 (13)	0.0665 (6)
H15	0.4994	0.7507	0.1053	0.080*
C16	0.6647 (2)	0.8214 (2)	0.07825 (12)	0.0652 (6)
H16	0.6398	0.9117	0.0739	0.078*
C17	0.7850 (2)	0.7855 (2)	0.06608 (13)	0.0611 (6)
H17	0.8416	0.8512	0.0536	0.073*
C18	0.8220 (2)	0.65176 (19)	0.07231 (12)	0.0521 (5)
H18	0.9040	0.6275	0.0644	0.063*
C19	0.80126 (16)	0.32140 (18)	0.00578 (9)	0.0386 (4)
C20	0.81954 (17)	0.18333 (19)	−0.00175 (10)	0.0418 (4)
C21	0.82192 (19)	0.1214 (2)	−0.07811 (12)	0.0525 (5)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.1100 (5)	0.0475 (3)	0.0406 (3)	−0.0042 (3)	0.0089 (3)	0.0085 (2)
P1	0.0371 (2)	0.0304 (2)	0.0353 (2)	−0.00044 (18)	0.00313 (17)	−0.00018 (18)
F1	0.1431 (15)	0.0604 (9)	0.0902 (11)	0.0336 (9)	0.0037 (10)	−0.0309 (8)
F2	0.0929 (11)	0.1209 (13)	0.0847 (10)	−0.0327 (10)	0.0504 (9)	−0.0435 (10)
F3	0.0673 (9)	0.1004 (12)	0.0743 (9)	0.0046 (8)	−0.0140 (7)	−0.0376 (8)
O1	0.0781 (10)	0.0360 (7)	0.0584 (9)	0.0046 (7)	0.0049 (7)	0.0034 (7)
C1	0.0387 (9)	0.0358 (9)	0.0386 (9)	−0.0042 (7)	0.0027 (7)	0.0051 (7)
C2	0.0450 (10)	0.0484 (11)	0.0537 (11)	0.0025 (9)	0.0015 (9)	0.0007 (9)
C3	0.0456 (12)	0.0732 (16)	0.0748 (16)	0.0104 (11)	−0.0030 (11)	0.0107 (13)
C4	0.0498 (12)	0.0874 (18)	0.0596 (14)	−0.0097 (12)	−0.0140 (10)	0.0165 (13)
C5	0.0659 (14)	0.0803 (17)	0.0468 (12)	−0.0170 (13)	−0.0082 (10)	−0.0055 (11)
C6	0.0518 (11)	0.0598 (13)	0.0493 (11)	−0.0040 (10)	0.0015 (9)	−0.0097 (10)
C7	0.0388 (9)	0.0391 (10)	0.0406 (9)	−0.0019 (7)	0.0051 (7)	−0.0004 (8)
C8	0.0484 (11)	0.0629 (13)	0.0435 (11)	−0.0055 (9)	0.0036 (8)	0.0053 (9)
C9	0.0659 (14)	0.0863 (17)	0.0503 (12)	−0.0117 (13)	0.0130 (10)	0.0173 (12)
C10	0.0581 (14)	0.0840 (18)	0.0720 (15)	−0.0201 (12)	0.0211 (12)	0.0103 (13)
C11	0.0504 (12)	0.0903 (18)	0.0693 (15)	−0.0253 (12)	0.0021 (11)	0.0004 (14)
C12	0.0508 (11)	0.0722 (15)	0.0469 (11)	−0.0143 (10)	−0.0006 (9)	0.0056 (10)

C13	0.0444 (10)	0.0347 (9)	0.0395 (9)	0.0047 (8)	−0.0007 (7)	−0.0031 (7)
C14	0.0520 (11)	0.0536 (12)	0.0539 (12)	0.0112 (9)	0.0070 (9)	0.0029 (10)
C15	0.0655 (14)	0.0674 (16)	0.0664 (14)	0.0315 (12)	0.0056 (11)	0.0000 (12)
C16	0.0926 (18)	0.0418 (12)	0.0572 (13)	0.0219 (12)	−0.0114 (12)	−0.0035 (10)
C17	0.0758 (15)	0.0361 (11)	0.0680 (14)	−0.0006 (10)	−0.0086 (11)	0.0006 (10)
C18	0.0528 (11)	0.0352 (10)	0.0673 (13)	−0.0002 (9)	0.0018 (10)	−0.0013 (9)
C19	0.0465 (10)	0.0346 (9)	0.0348 (9)	−0.0010 (7)	0.0055 (7)	0.0010 (7)
C20	0.0418 (10)	0.0375 (10)	0.0460 (10)	−0.0017 (8)	0.0043 (8)	−0.0050 (8)
C21	0.0469 (11)	0.0504 (12)	0.0605 (13)	0.0006 (9)	0.0070 (9)	−0.0163 (10)

Geometric parameters (Å, °)

Cl1—C19	1.7346 (18)	C8—C9	1.383 (3)
P1—C19	1.7509 (17)	C8—H8	0.9300
P1—C13	1.7984 (18)	C9—C10	1.366 (3)
P1—C1	1.8011 (17)	C9—H9	0.9300
P1—C7	1.8026 (18)	C10—C11	1.369 (3)
F1—C21	1.319 (3)	C10—H10	0.9300
F2—C21	1.318 (3)	C11—C12	1.376 (3)
F3—C21	1.327 (2)	C11—H11	0.9300
O1—C20	1.244 (2)	C12—H12	0.9300
C1—C2	1.377 (3)	C13—C14	1.381 (3)
C1—C6	1.393 (3)	C13—C18	1.392 (3)
C2—C3	1.382 (3)	C14—C15	1.388 (3)
C2—H2	0.9300	C14—H14	0.9300
C3—C4	1.368 (3)	C15—C16	1.370 (4)
C3—H3	0.9300	C15—H15	0.9300
C4—C5	1.369 (4)	C16—C17	1.368 (3)
C4—H4	0.9300	C16—H16	0.9300
C5—C6	1.384 (3)	C17—C18	1.377 (3)
C5—H5	0.9300	C17—H17	0.9300
C6—H6	0.9300	C18—H18	0.9300
C7—C8	1.382 (3)	C19—C20	1.384 (3)
C7—C12	1.385 (3)	C20—C21	1.533 (3)
C19—P1—C13	108.54 (8)	C10—C11—C12	120.1 (2)
C19—P1—C1	113.87 (8)	C10—C11—H11	120.0
C13—P1—C1	106.25 (8)	C12—C11—H11	120.0
C19—P1—C7	109.72 (8)	C11—C12—C7	120.5 (2)
C13—P1—C7	108.90 (9)	C11—C12—H12	119.8
C1—P1—C7	109.40 (8)	C7—C12—H12	119.8
C2—C1—C6	119.66 (17)	C14—C13—C18	119.39 (18)
C2—C1—P1	120.37 (14)	C14—C13—P1	122.15 (15)
C6—C1—P1	119.98 (14)	C18—C13—P1	118.44 (14)
C1—C2—C3	119.8 (2)	C13—C14—C15	119.5 (2)
C1—C2—H2	120.1	C13—C14—H14	120.2
C3—C2—H2	120.1	C15—C14—H14	120.2
C4—C3—C2	120.5 (2)	C16—C15—C14	120.4 (2)
C4—C3—H3	119.8	C16—C15—H15	119.8
C2—C3—H3	119.8	C14—C15—H15	119.8

C3—C4—C5	120.4 (2)	C17—C16—C15	120.4 (2)
C3—C4—H4	119.8	C17—C16—H16	119.8
C5—C4—H4	119.8	C15—C16—H16	119.8
C4—C5—C6	120.0 (2)	C16—C17—C18	119.9 (2)
C4—C5—H5	120.0	C16—C17—H17	120.1
C6—C5—H5	120.0	C18—C17—H17	120.1
C5—C6—C1	119.7 (2)	C17—C18—C13	120.3 (2)
C5—C6—H6	120.1	C17—C18—H18	119.8
C1—C6—H6	120.1	C13—C18—H18	119.8
C8—C7—C12	119.16 (17)	C20—C19—Cl1	124.21 (14)
C8—C7—P1	122.19 (14)	C20—C19—P1	115.94 (14)
C12—C7—P1	118.64 (14)	Cl1—C19—P1	119.81 (10)
C7—C8—C9	119.64 (19)	O1—C20—C19	123.49 (17)
C7—C8—H8	120.2	O1—C20—C21	116.56 (17)
C9—C8—H8	120.2	C19—C20—C21	119.95 (17)
C10—C9—C8	120.8 (2)	F2—C21—F1	107.12 (18)
C10—C9—H9	119.6	F2—C21—F3	105.66 (19)
C8—C9—H9	119.6	F1—C21—F3	105.25 (18)
C9—C10—C11	119.9 (2)	F2—C21—C20	113.74 (17)
C9—C10—H10	120.1	F1—C21—C20	111.79 (18)
C11—C10—H10	120.1	F3—C21—C20	112.67 (16)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···O1	0.93	2.50	3.1460	127
C17—H17···O1^{i}	0.93	2.49	3.1937	133

Symmetry codes: (i) *x*, *y*+1, *z*.

Fig. 1

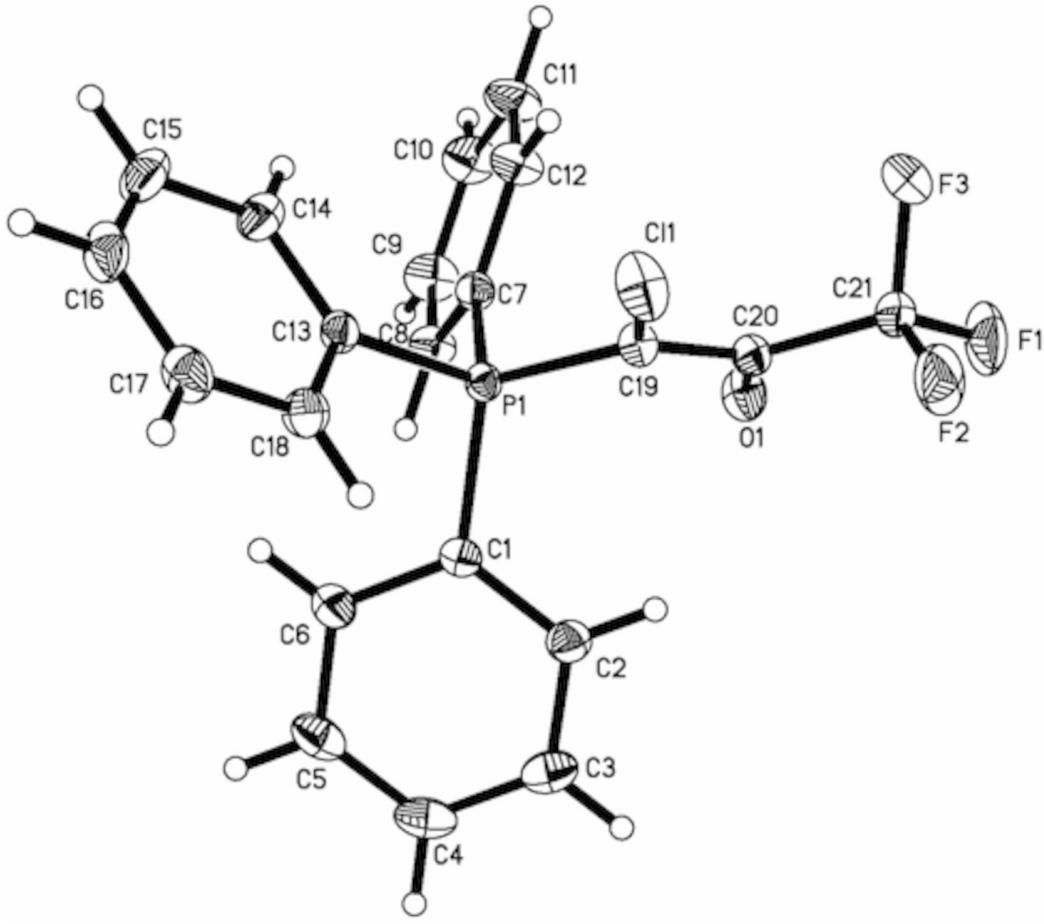
C11
C15
C10
C12
F3
C14
C9
Cl1
C7
C21
C16
C13
C8
C20
F1
C17
P1
C19
O1
F2
C18
C1
C6
C2
C5
C3
C4

Fig. 2

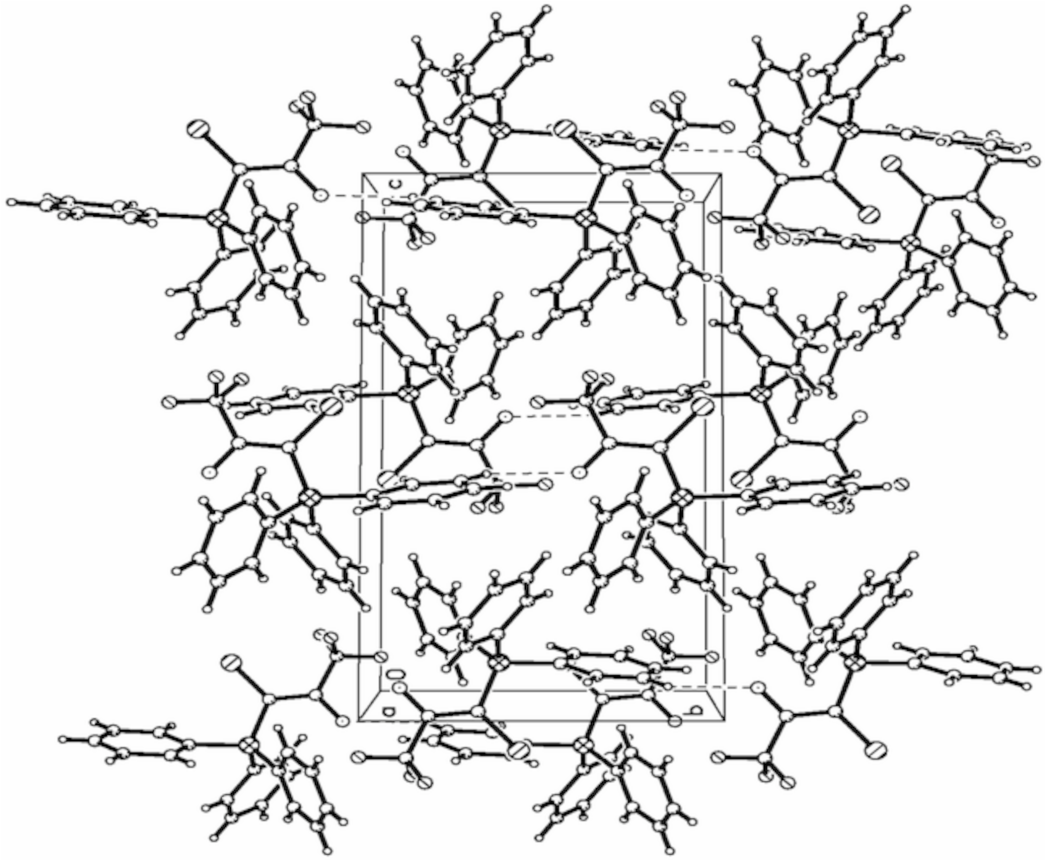

Fig. 3