

2-[(2,4,4,6,6-Pentachloro-1,3,5,2λ⁵,4λ⁵,-6λ⁵-triazatriphosphinin-2-yl)azanidyl]-pyridinium

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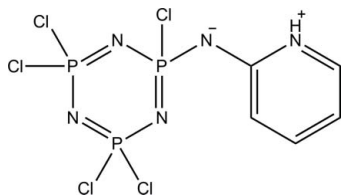
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.023; wR factor = 0.061; data-to-parameter ratio = 31.4.

The title compound, $\text{C}_5\text{H}_5\text{Cl}_5\text{N}_5\text{P}_3$, crystallizes as a zwitterion in which the pyridine N atom is protonated. An $S(6)$ ring motif is formed *via* an intramolecular $\text{C}-\text{H}\cdots\text{N}$ hydrogen bond. The triazatriphosphinin ring adopts an envelope conformation, with one N atom displaced by 0.145 (1) Å from the other atoms. In the crystal, $\text{N}-\text{H}\cdots\text{N}$ and $\text{C}-\text{H}\cdots\text{N}$ hydrogen bonds link the molecules into centrosymmetric dimers containing one $R_2^2(7)$ ring motif and two $R_2^2(8)$ ring motifs.

Related literature

For background to the reactions of hexachlorocyclo-triphosphazene, see: Polder & Wagner (1976). For a related structure, see: Coles *et al.* (2007). For ring conformations, see: Cremer & Pople (1975). For the stability of the temperature controller used in the data collection, see: Cosier & Glazer (1986).



Experimental

Crystal data

 $\text{C}_5\text{H}_5\text{Cl}_5\text{N}_5\text{P}_3$
 $M_r = 405.30$

Monoclinic, $P2_1/c$
 $a = 8.8677$ (1) Å
 $b = 14.7225$ (2) Å
 $c = 12.3564$ (2) Å
 $\beta = 119.355$ (1)°
 $V = 1406.05$ (3) Å³

$Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 1.36$ mm⁻¹
 $T = 100$ K
 $0.59 \times 0.38 \times 0.36$ mm

Data collection

Bruker SMART APEXII CCD diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2009)
 $T_{\min} = 0.499$, $T_{\max} = 0.640$

19432 measured reflections
 5116 independent reflections
 4806 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.017$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.023$
 $wR(F^2) = 0.061$
 $S = 1.09$
 5116 reflections

163 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.54$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.39$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---|-------|-------------|-------------|---------------|
| $\text{N5}-\text{H1}\cdots\text{N4}^i$ | 0.84 | 2.16 | 2.9949 (14) | 177 |
| $\text{C2}-\text{H2A}\cdots\text{N3}$ | 0.93 | 2.55 | 3.1538 (19) | 123 |
| $\text{C5}-\text{H5A}\cdots\text{N1}^i$ | 0.93 | 2.50 | 3.2220 (16) | 135 |

Symmetry code: (i) $-x + 2, -y, -z + 1$.

Data collection: APEX2 (Bruker, 2009); cell refinement: SAINT (Bruker, 2009); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL and PLATON (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB6587).

References

- Bruker (2009). APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
 Coles, S. J., Davies, D. B., Hursthouse, M. B., İbişoğlu, H., Kılıç, A. & Shaw, R. A. (2007). *Acta Cryst.* **E63**, o3753.
 Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.
 Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
 Polder, W. & Wagner, A. J. (1976). *Cryst. Struct. Commun.* **5**, 253–257.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
 Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.

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supplementary materials

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2-[(2,4,4,6,6-Pentachloro-1,3,5,2 λ^5 ,4 λ^5 ,6 λ^5 -triazatriphosphinin-2-yl)azanidyl]pyridinium

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Comment

Hexachlorocyclotriphosphazene is an inorganic six-membered cyclic compound consisting of alternating phosphorous and nitrogen atoms. It can also be considered as a trimer of azaphosphoryldichloride (NPCl₂), which can be readily formed by the reaction of phosphorous pentachloride and ammonium chloride in chlorobenzene. The results of the reaction of phosphazene derivatives with nucleophile reagent strongly depend on reaction conditions whereas a series of various substitution derivatives can be formed (e.g. Polder & Wagner, 1976).

The title compound (Fig. 1), crystallizes as a zwitterion in which the pyridine N atom is protonated. An *S*(6) ring motif is formed *via* an intramolecular C2—H2A \cdots N3 hydrogen bond (Table 1). The triazatriphosphinine ring (P1/N2/P2/N3/P3/N1) adopts an envelope conformation with the puckering parameters (Cremer & Pople, 1975), $Q = 0.2087 \text{ \AA}$; $\Theta = 138.0 (2)^\circ$; $\varphi = 3.7 (4)^\circ$ and it is comparable to a related structure (Coles *et al.*, 2007). In the crystal (Fig. 2), N5—H1 \cdots N4 and C5—H5A \cdots N1 hydrogen bonds (Table 1) link the molecules to form one $R^2_2(7)$ ring motif and two $R^2_2(8)$ ring motifs.

Experimental

Hexachlorocyclotriphosphazene (0.5 g, 0.07 mol), 2-aminopyridine (0.26 g, 0.14 mol) and triethyl amine (0.14 g, 0.07 mol) were stirred in acetone at -80°C in liquid nitrogen bath for 5 h under anhydrous conditions. The obtained triethylammonium-chloride was filtered off under nitrogen and washed with fresh acetone and the solvent reduced to the minimum. Further, 10 ml of dried acetone was added the yield of the title product after deep freezing crystallization was about 60–66%. Colourless blocks were obtained by the slow evaporation of solvent at freezing temperature of acetone. *M.p.*: 455 K.

Refinement

The N-bound hydrogen atom was located from the difference Fourier map and was fixed at their found positions with a riding model with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{N})$ [N—H = 0.8354 Å]. The remaining hydrogen atoms were positioned geometrically and were refined with a riding model with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ [C—H = 0.93 Å]. Four outliers were omitted for the final refinement, 3 16 4, 3 19 6, -3 16 7 and -3 19 9.

Figures

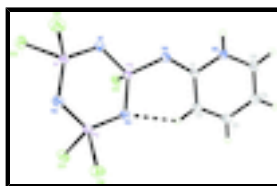


Fig. 1. The molecular structure of the title compound, showing 50% probability displacement ellipsoids. The dashed line indicates the intramolecular hydrogen bond.

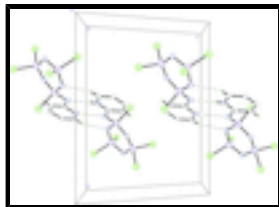


Fig. 2. The crystal packing of the title compound, viewed along the *a* axis. H atoms not involved in the intermolecular interactions (dashed lines) have been omitted for clarity.

2-[(2,4,4,6,6-Pentachloro-1,3,5,2λ⁵,4λ⁵,6λ⁵-triazatriphosphinin- 2-yl)azanidyl]pyridinium

Crystal data

| | |
|---------------------------------|---|
| $C_5H_5Cl_5N_5P_3$ | $F(000) = 800$ |
| $M_r = 405.30$ | $D_x = 1.915 \text{ Mg m}^{-3}$ |
| Monoclinic, $P2_1/c$ | Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$ |
| Hall symbol: -P 2ybc | Cell parameters from 9860 reflections |
| $a = 8.8677 (1) \text{ \AA}$ | $\theta = 2.4\text{--}32.6^\circ$ |
| $b = 14.7225 (2) \text{ \AA}$ | $\mu = 1.36 \text{ mm}^{-1}$ |
| $c = 12.3564 (2) \text{ \AA}$ | $T = 100 \text{ K}$ |
| $\beta = 119.355 (1)^\circ$ | Block, colourless |
| $V = 1406.05 (3) \text{ \AA}^3$ | $0.59 \times 0.38 \times 0.36 \text{ mm}$ |
| $Z = 4$ | |

Data collection

| | |
|---|--|
| Bruker SMART APEXII CCD diffractometer | 5116 independent reflections |
| Radiation source: fine-focus sealed tube graphite | 4806 reflections with $I > 2\sigma(I)$ |
| φ and ω scans | $R_{\text{int}} = 0.017$ |
| Absorption correction: multi-scan (<i>SADABS</i> ; Bruker, 2009) | $\theta_{\text{max}} = 32.6^\circ$, $\theta_{\text{min}} = 2.3^\circ$ |
| $T_{\text{min}} = 0.499$, $T_{\text{max}} = 0.640$ | $h = -11 \rightarrow 13$ |
| 19432 measured reflections | $k = -22 \rightarrow 19$ |
| | $l = -18 \rightarrow 18$ |

Refinement

| | |
|---------------------------------|--|
| Refinement on F^2 | Primary atom site location: structure-invariant direct methods |
| Least-squares matrix: full | Secondary atom site location: difference Fourier map |
| $R[F^2 > 2\sigma(F^2)] = 0.023$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.061$ | H-atom parameters constrained |
| $S = 1.09$ | $w = 1/[\sigma^2(F_o^2) + (0.0211P)^2 + 1.0751P]$ |
| 5116 reflections | where $P = (F_o^2 + 2F_c^2)/3$ |
| 163 parameters | $(\Delta/\sigma)_{\text{max}} = 0.001$ |
| 0 restraints | $\Delta\rho_{\text{max}} = 0.54 \text{ e \AA}^{-3}$ |
| | $\Delta\rho_{\text{min}} = -0.39 \text{ e \AA}^{-3}$ |

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cryosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1) K.

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 $F^2 > \sigma(F^2)$ 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 (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|---------------|--------------|----------------------------------|
| C11 | 1.37616 (5) | 0.29414 (2) | 0.46163 (3) | 0.02552 (7) |
| C12 | 1.44578 (4) | 0.19325 (3) | 0.27089 (3) | 0.02419 (7) |
| C13 | 0.89064 (4) | 0.22782 (2) | -0.05598 (3) | 0.02220 (7) |
| C14 | 0.77111 (4) | 0.35825 (2) | 0.08438 (3) | 0.02138 (6) |
| C15 | 0.99461 (4) | -0.00326 (2) | 0.13895 (3) | 0.01986 (6) |
| P1 | 1.25273 (4) | 0.22143 (2) | 0.30552 (3) | 0.01580 (6) |
| P2 | 0.92671 (4) | 0.25229 (2) | 0.11553 (3) | 0.01506 (6) |
| P3 | 0.99248 (4) | 0.09616 (2) | 0.25490 (3) | 0.01336 (6) |
| N1 | 1.18802 (13) | 0.13083 (8) | 0.33652 (9) | 0.01774 (19) |
| N2 | 1.12016 (15) | 0.28591 (8) | 0.19854 (10) | 0.0216 (2) |
| N3 | 0.85908 (13) | 0.17106 (8) | 0.16243 (9) | 0.01651 (18) |
| N4 | 0.93798 (13) | 0.04813 (7) | 0.34645 (9) | 0.01398 (17) |
| N5 | 0.75893 (13) | -0.03097 (7) | 0.39730 (9) | 0.01419 (17) |
| H1 | 0.8457 | -0.0360 | 0.4677 | 0.017* |
| C1 | 0.78001 (15) | 0.01276 (8) | 0.30878 (10) | 0.01275 (18) |
| C2 | 0.63220 (16) | 0.01682 (9) | 0.18857 (10) | 0.0171 (2) |
| H2A | 0.6394 | 0.0459 | 0.1244 | 0.021* |
| C3 | 0.47895 (16) | -0.02188 (10) | 0.16644 (11) | 0.0200 (2) |
| H3A | 0.3833 | -0.0190 | 0.0873 | 0.024* |
| C4 | 0.46472 (16) | -0.06569 (10) | 0.26157 (11) | 0.0212 (2) |
| H4A | 0.3608 | -0.0916 | 0.2469 | 0.025* |
| C5 | 0.60793 (16) | -0.06919 (9) | 0.37649 (11) | 0.0190 (2) |
| H5A | 0.6018 | -0.0981 | 0.4412 | 0.023* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|--------------|--------------|---------------|--------------|---------------|
| C11 | 0.02946 (16) | 0.02404 (16) | 0.01697 (12) | -0.00508 (12) | 0.00667 (11) | -0.00396 (11) |
| C12 | 0.02044 (14) | 0.03211 (18) | 0.02312 (13) | -0.00176 (12) | 0.01309 (11) | 0.00253 (12) |
| C13 | 0.02719 (15) | 0.02464 (15) | 0.01649 (12) | -0.00050 (12) | 0.01203 (11) | 0.00132 (10) |

supplementary materials

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|-----|--------------|--------------|--------------|---------------|--------------|---------------|
| Cl4 | 0.02328 (14) | 0.01568 (13) | 0.02180 (13) | 0.00245 (10) | 0.00843 (11) | 0.00085 (10) |
| Cl5 | 0.02308 (14) | 0.02248 (15) | 0.01536 (11) | 0.00251 (11) | 0.01046 (10) | -0.00064 (10) |
| P1 | 0.01431 (13) | 0.01830 (15) | 0.01237 (12) | -0.00312 (11) | 0.00467 (10) | 0.00161 (10) |
| P2 | 0.01528 (13) | 0.01473 (14) | 0.01295 (12) | -0.00074 (10) | 0.00522 (10) | 0.00284 (10) |
| P3 | 0.01322 (12) | 0.01484 (14) | 0.01122 (11) | -0.00054 (10) | 0.00537 (9) | 0.00243 (9) |
| N1 | 0.0139 (4) | 0.0200 (5) | 0.0156 (4) | -0.0022 (4) | 0.0043 (3) | 0.0049 (4) |
| N2 | 0.0172 (5) | 0.0210 (5) | 0.0194 (4) | -0.0042 (4) | 0.0035 (4) | 0.0070 (4) |
| N3 | 0.0144 (4) | 0.0170 (5) | 0.0160 (4) | 0.0001 (4) | 0.0058 (3) | 0.0054 (3) |
| N4 | 0.0145 (4) | 0.0157 (4) | 0.0117 (4) | -0.0018 (3) | 0.0063 (3) | 0.0015 (3) |
| N5 | 0.0137 (4) | 0.0160 (5) | 0.0116 (4) | -0.0016 (3) | 0.0053 (3) | 0.0008 (3) |
| C1 | 0.0149 (5) | 0.0120 (5) | 0.0117 (4) | 0.0001 (4) | 0.0067 (4) | -0.0003 (3) |
| C2 | 0.0157 (5) | 0.0227 (6) | 0.0115 (4) | -0.0004 (4) | 0.0055 (4) | 0.0017 (4) |
| C3 | 0.0157 (5) | 0.0275 (6) | 0.0135 (4) | -0.0016 (5) | 0.0045 (4) | 0.0007 (4) |
| C4 | 0.0156 (5) | 0.0282 (7) | 0.0172 (5) | -0.0055 (5) | 0.0059 (4) | 0.0005 (4) |
| C5 | 0.0172 (5) | 0.0228 (6) | 0.0162 (5) | -0.0041 (4) | 0.0075 (4) | 0.0028 (4) |

Geometric parameters (Å, °)

| | | | |
|------------|--------------|-----------|-------------|
| Cl1—P1 | 1.9987 (4) | N4—C1 | 1.3456 (15) |
| Cl2—P1 | 2.0011 (5) | N5—C5 | 1.3558 (16) |
| Cl3—P2 | 2.0146 (4) | N5—C1 | 1.3589 (14) |
| Cl4—P2 | 1.9912 (5) | N5—H1 | 0.8354 |
| Cl5—P3 | 2.0548 (4) | C1—C2 | 1.4209 (15) |
| P1—N1 | 1.5719 (11) | C2—C3 | 1.3718 (18) |
| P1—N2 | 1.5834 (11) | C2—H2A | 0.9300 |
| P2—N3 | 1.5705 (11) | C3—C4 | 1.3996 (18) |
| P2—N2 | 1.5858 (11) | C3—H3A | 0.9300 |
| P3—N4 | 1.5967 (10) | C4—C5 | 1.3652 (17) |
| P3—N1 | 1.6031 (11) | C4—H4A | 0.9300 |
| P3—N3 | 1.6111 (11) | C5—H5A | 0.9300 |
| N1—P1—N2 | 120.13 (6) | P2—N3—P3 | 120.16 (7) |
| N1—P1—Cl1 | 108.18 (4) | C1—N4—P3 | 123.48 (8) |
| N2—P1—Cl1 | 108.41 (5) | C5—N5—C1 | 123.83 (10) |
| N1—P1—Cl2 | 109.20 (5) | C5—N5—H1 | 118.7 |
| N2—P1—Cl2 | 107.98 (5) | C1—N5—H1 | 117.4 |
| Cl1—P1—Cl2 | 101.32 (2) | N4—C1—N5 | 115.82 (10) |
| N3—P2—N2 | 119.12 (6) | N4—C1—C2 | 128.01 (10) |
| N3—P2—Cl4 | 108.31 (4) | N5—C1—C2 | 116.17 (10) |
| N2—P2—Cl4 | 107.93 (5) | C3—C2—C1 | 120.46 (11) |
| N3—P2—Cl3 | 111.07 (4) | C3—C2—H2A | 119.8 |
| N2—P2—Cl3 | 107.45 (5) | C1—C2—H2A | 119.8 |
| Cl4—P2—Cl3 | 101.487 (19) | C2—C3—C4 | 120.82 (11) |
| N4—P3—N1 | 107.76 (5) | C2—C3—H3A | 119.6 |
| N4—P3—N3 | 115.69 (6) | C4—C3—H3A | 119.6 |
| N1—P3—N3 | 114.83 (6) | C5—C4—C3 | 118.04 (12) |
| N4—P3—Cl5 | 106.73 (4) | C5—C4—H4A | 121.0 |
| N1—P3—Cl5 | 106.78 (5) | C3—C4—H4A | 121.0 |
| N3—P3—Cl5 | 104.34 (4) | N5—C5—C4 | 120.68 (11) |
| P1—N1—P3 | 121.89 (7) | N5—C5—H5A | 119.7 |

| | | | |
|--------------|-------------|--------------|--------------|
| P1—N2—P2 | 118.55 (7) | C4—C5—H5A | 119.7 |
| N2—P1—N1—P3 | 5.48 (12) | N1—P3—N3—P2 | 24.81 (10) |
| Cl1—P1—N1—P3 | 130.57 (7) | Cl5—P3—N3—P2 | -91.71 (7) |
| Cl2—P1—N1—P3 | -119.97 (7) | N1—P3—N4—C1 | 178.60 (10) |
| N4—P3—N1—P1 | -144.81 (8) | N3—P3—N4—C1 | 48.55 (12) |
| N3—P3—N1—P1 | -14.28 (11) | Cl5—P3—N4—C1 | -67.03 (10) |
| Cl5—P3—N1—P1 | 100.84 (8) | P3—N4—C1—N5 | 175.77 (9) |
| N1—P1—N2—P2 | -6.08 (12) | P3—N4—C1—C2 | -5.33 (18) |
| Cl1—P1—N2—P2 | -131.06 (7) | C5—N5—C1—N4 | 178.77 (12) |
| Cl2—P1—N2—P2 | 119.94 (7) | C5—N5—C1—C2 | -0.27 (18) |
| N3—P2—N2—P1 | 16.53 (12) | N4—C1—C2—C3 | -178.84 (13) |
| Cl4—P2—N2—P1 | 140.46 (7) | N5—C1—C2—C3 | 0.06 (18) |
| Cl3—P2—N2—P1 | -110.81 (8) | C1—C2—C3—C4 | 0.3 (2) |
| N2—P2—N3—P3 | -26.66 (11) | C2—C3—C4—C5 | -0.4 (2) |
| Cl4—P2—N3—P3 | -150.41 (6) | C1—N5—C5—C4 | 0.1 (2) |
| Cl3—P2—N3—P3 | 98.96 (7) | C3—C4—C5—N5 | 0.2 (2) |
| N4—P3—N3—P2 | 151.37 (7) | | |

Hydrogen-bond geometry (Å, °)

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|--------------------------|-------------|---------------|-----------------------|-------------------------|
| N5—H1...N4 ⁱ | 0.84 | 2.16 | 2.9949 (14) | 177 |
| C2—H2A...N3 | 0.93 | 2.55 | 3.1538 (19) | 123 |
| C5—H5A...N1 ⁱ | 0.93 | 2.50 | 3.2220 (16) | 135 |

Symmetry codes: (i) $-x+2, -y, -z+1$.

Fig. 1

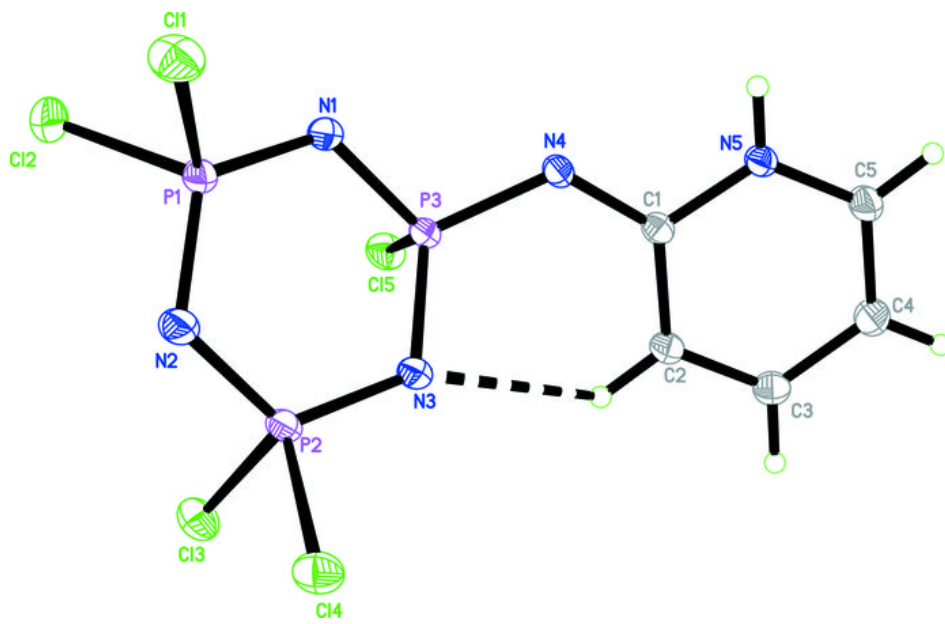


Fig. 2

