Crystal Structure of Spirocyclic Pentaerythritol Phenol Ester of Phosphoric Acid

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Abstract Spirocyclic pentaerythritol phosphate ester, a kind of intumescent flame retardant, has good compatibility with the polypropylene and excellent flame retardant on PP. However the correlation between the space structures of the intumescent flame retardant and polypropylene has not been revealed. In this paper crystal diffraction of spirocyclic pentaerythritol phenol ester of phosphoric acid are used to study its structure features and the results show that the phenol ester crystal is orthorhombic, Pna21 space group, and there are two six-member rings linked to the same atom which belongs to similar chair conformation forming a stable spiro structure and an irregular axisymmetric structure, and none weak hydrogen bonds exists in the system.

1. Introduction
Flame retardant is an additive to delay time of ignition and inhibit flame propagation.[1] It could be used in most polymer materials, such as plastics, fibres, rubber, wood, paper and paint. Rational use of flame retardants can effectively improve the flame retardant properties of the materials. Recently, the researches of flame retardant has focused on intumescent flame retardant [2], which has low smoke, low toxicity and environment-friendly.[3, 4] The compounds can greatly reduce the flammability of polymer materials. Spirocyclic pentaerythritol phenol ester of phosphoric acid (SPEPA) is a kind of intumescent flame retardants [5]. Adding large amount traditional inorganic flame retardant or organic flame retardant can reach the ideal flame retardant of the polypropylene (PP), however the material’s physical and mechanical properties of PP could be deteriorated [6]. The spirocyclic phosphoramidate [7] has excellent flame retardant on PP and well compatibility with PP. It is related with the molecular space structure of spirocyclic phosphoramidate. In this paper, the main work has been focused on the crystal structure of the SPEPA.

2. Experimental Procedure

2.1 Materials
The spiralphosphodicholor (SPDPC) was synthesized by pentaerythritol and phosphorus oxychloride in the laboratory containing two highly active functional groups in both ends, which was white powder and the melting point (M.P) was 234-236 °C.

Spirocyclic pentaerythritol phenol ester of phosphoric acid (SPEPA) was obtained according to previous work. Yield: phosphate (3.6 g, 87.37 %), M.P 203-204 °C, Elemental analysis (Found: P, 15.12 %. Calc. for C₁₇H₁₈O₈P₂: 15.03 %), IR absorption (KBr pellets) νmax/cm⁻¹: 1150 and 1040 (P-O), 953 (P-OAr), 1190 [P-O (-C₆H₄)], 922, 851, 775 and 685 (the characteristic infrared absorption peaks of the spiro), 766 and 688 (the IR absorption of mono-substituted benzene). ¹H-NMR (300MHz, CDCl₃) δ: 7.22-7.40(10H, ArH), 4.89-4.78, 4.51-4.56, 4.10-4.31(8H, CH₂).

2.2 Preparation of the crystals of SPEPA
Crystals of SPEPA were obtained by slow diffusion of dichloromethane with saturated acetone solution at room temperature for one week, which are sheet-like crystals.

2.3 Characterization
The structure determination and refinement of the crystal were evaluated on a Bruker Smart-1000 CCD X-ray diffractometer equipped with a graphite-monochromated MoKα radiation (λ= 0.071073 nm) using a ω-2θ scan mode at 275(2) K, the total of 27513 (Rint = 0.0386) diffraction data was collected in the range of 3.11° < θ < 27.48°.

3. Results and discussion
3.1 The crystals structure of SPEPA
The molecular structure of SPEPA with atom label is shown in Figure 1. The molecular formula of SPEPA is C₁₇H₁₈O₈P₂ and the atomic number can be observed in Figure 1.

P atom of SPEPA adopts the sp³ hybrid orbit. The bond and the torsion angles data is shown in Table 1 and Table 2, respectively. The O(1), O(2), O(3) and O(4) atom linked to P(1) atom form slight distortion tetrahedron, the angle of O(2)-P(1)-O(4) is 106.50(10)° which almost equal to the criterion tetrahedron (109°28'). However, the angles of O(1)-P(1)-O(3), O(1)-P(1)-O(4) and O(1)-P(1)-O(2) are 114.12(11)°, 111.84° and 116.22°, which are obviously greater than those angles of O(3)-P(1)-O(4) (105.37(9)°), O(3)-P(1)-O(2) (101.70(9)°) and O(4)-P(1)-O(2) (106.50(10)°). This may be due to the great polarity of P=O and the around conditions.

Figure 1 The molecular structure with atom label of the SPEPA.
| Three atomic bond | Angle(°)  | Three atomic bond | Angle(°)  |
|------------------|-----------|------------------|-----------|
| O(1)-P(1)-O(3)   | 114.12(11)| C(11)-C(8)-C(9)  | 112.47(17)|
| O(1)-P(1)-O(4)   | 111.84(12)| C(11)-C(8)-C(10)| 108.99(18)|
| O(3)-P(1)-O(4)   | 105.37(9) | C(9)-C(8)-C(10)| 108.90(18)|
| O(1)-P(1)-O(2)   | 116.22(10)| C(11)-C(8)-C(7) | 109.10(17)|
| O(3)-P(1)-O(2)   | 101.70(9) | C(9)-C(8)-C(7)  | 109.53(18)|
| O(4)-P(1)-O(2)   | 106.50(10)| C(10)-C(8)-C(7)| 107.73(17)|
| O(5)-P(2)-O(8)   | 114.60(11)| O(3)-C(9)-C(8)  | 110.72(16)|
| O(5)-P(2)-O(7)   | 112.22(11)| O(3)-C(9)-H(9A)| 109.5    |
| O(8)-P(2)-O(7)   | 105.49(9) | C(8)-C(9)-H(9A)| 109.5    |
| O(5)-P(2)-O(6)   | 115.79(10)| O(3)-C(9)-H(9B)| 109.5    |
| O(8)-P(2)-O(6)   | 101.62(10)| C(8)-C(9)-H(9B)| 109.5    |
| O(7)-P(2)-O(6)   | 105.99(10)| H(9A)-C(9)-H(9B)| 108.1    |
| C(1)-O(2)-P(1)   | 122.31(14)| O(7)-C(10)-C(8)| 110.66(17)|
| C(9)-O(3)-P(1)   | 117.98(13)| O(7)-C(10)-H(10A)| 109.5 |
| C(7)-O(4)-P(1)   | 119.87(14)| O(8)-C(11)-H(11A)| 109.4 |
| C(12)-O(6)-P(2)  | 121.77(14)| O(7)-C(10)-H(10B)| 109.5 |
| C(10)-O(7)-P(2)  | 119.32(13)| C(8)-C(10)-H(10B)| 109.5 |
| C(11)-O(8)-P(2)  | 118.56(13)| H(10A)-C(10)-H(10B)| 108.1 |
| C(2)-C(1)-C(6)   | 121.8(3)  | O(8)-C(11)-H(11B)| 109.4 |
| C(2)-C(1)-O(2)   | 117.6(2)  | O(8)-C(11)-H(11A)| 109.4 |
| C(6)-C(1)-O(2)   | 120.6(2)  | C(8)-C(11)-H(11A)| 109.4 |
| C(1)-C(2)-C(3)   | 118.8(3)  | O(8)-C(11)-H(11B)| 109.4 |
| C(1)-C(2)-H(2A)  | 120.6     | C(8)-C(11)-H(11B)| 109.4 |
| C(3)-C(2)-H(2A)  | 120.6     | H(11A)-C(11)-H(11B)| 108.0 |
| C(4)-C(3)-C(2)   | 120.2(3)  | C(13)-C(12)-C(17)| 122.3(2) |
| C(4)-C(3)-H(3A)  | 119.9     | C(13)-C(12)-O(6)| 118.0(2) |
| C(2)-C(3)-H(3A)  | 119.9     | C(17)-C(12)-O(6)| 119.6(2) |
| C(5)-C(4)-C(3)   | 120.3(3)  | C(12)-C(13)-C(14)| 118.4(3) |
| C(5)-C(4)-H(4A)  | 119.8     | C(12)-C(13)-H(13A)| 120.8 |
| C(3)-C(4)-H(4A)  | 119.8     | C(14)-C(13)-H(13A)| 120.8 |
| C(4)-C(5)-C(6)   | 120.6(3)  | C(15)-C(14)-C(13)| 119.7(3) |
| C(4)-C(5)-H(5A)  | 119.7     | C(15)-C(14)-H(14A)| 120.2 |
| C(6)-C(5)-H(5A)  | 119.7     | C(13)-C(14)-H(14A)| 120.2 |
| C(1)-C(6)-C(5)   | 118.3(3)  | C(16)-C(15)-C(14)| 121.0(3) |
| C(1)-C(6)-H(6A)  | 120.9     | C(16)-C(15)-H(15A)| 119.5 |
| C(5)-C(6)-H(6A)  | 120.9     | C(14)-C(15)-H(15A)| 119.5 |
| O(4)-C(7)-C(8)   | 110.09(17)| C(15)-C(16)-C(17)| 119.9(3) |
| O(4)-C(7)-H(7A)  | 109.6     | C(15)-C(16)-H(16A)| 120.1 |
| C(8)-C(7)-H(7A)  | 109.6     | C(17)-C(16)-H(16A)| 120.1 |
| O(4)-C(7)-H(7B)  | 109.6     | C(12)-C(17)-C(16)| 118.7(3) |
| C(8)-C(7)-H(7B)  | 109.6     | C(12)-C(17)-H(17A)| 120.6 |
| H(7A)-C(7)-H(7B) | 108.2     | C(16)-C(17)-H(17A)| 120.6 |
Table 2 Torsional angles for the SPEPA

| Four atomic bond | Torsional angle(°) | Four atomic bond | Torsional angle(°) |
|------------------|--------------------|------------------|--------------------|
| O1—P1—O2—C1     | -54.7(2)           | C4—C5—C6—C1     | 0.4(5)             |
| O3—P1—O2—C1     | -179.29(17)        | P1—O4—C7—C8     | 52.3(3)            |
| O4—P1—O2—C1     | 70.61(18)          | O4—C7—C8—C11    | 66.9(2)            |
| O1—P1—O3—C9     | 167.63(17)         | O4—C7—C8—C9     | -56.6(2)           |
| O4—P1—O3—C9     | 44.54(18)          | O4—C7—C8—C10    | -174.92(19)        |
| O2—P1—O3—C9     | -66.42(17)         | P1—O3—C9—C8     | -55.9(2)           |
| O1—P1—O4—C7     | -168.04(17)        | C11—C8—C9—O3    | -62.6(2)           |
| O3—P1—O4—C7     | -43.51(19)         | C10—C8—C9—O3    | 176.53(17)         |
| O2—P1—O4—C7     | 63.99(19)          | C7—C8—C9—O3     | 58.9(2)            |
| O5—P2—O6—C12    | -52.1(2)           | P2—O7—C10—C8    | 53.0(2)            |
| O8—P2—O6—C12    | -176.89(18)        | C11—C8—C10—O7   | -57.4(2)           |
| O7—P2—O6—C12    | 73.07(19)          | C9—C8—C10—O7    | 65.6(2)            |
| O5—P2—O7—C10    | -168.32(16)        | C7—C8—C10—O7    | -175.68(18)        |
| O8—P2—O7—C10    | -42.88(18)         | P2—O8—C11—C8    | -54.7(2)           |
| O6—P2—O7—C10    | 64.39(17)          | C9—C8—C11—O8    | -62.5(2)           |
| O5—P2—O8—C11    | 167.16(17)         | C10—C8—C11—O8   | 58.4(2)            |
| O7—P2—O8—C11    | 43.22(18)          | C7—C8—C11—O8    | 175.80(17)         |
| O6—P2—O8—C11    | -67.20(18)         | P2—O6—C12—C13   | -112.3(2)          |
| P1—O2—C1—C2     | -116.3(2)          | P2—O6—C12—C17   | 70.0(3)            |
| P1—O2—C1—C6     | 65.6(3)            | C17—C12—C13—C14 | -1.2(4)            |
| C6—C1—C2—C3     | 0.3(4)             | O6—C12—C13—C14  | -178.9(2)          |
| O2—C1—C2—C3     | -177.8(3)          | C12—C13—C14—C15 | 0.5(4)             |
| C1—C2—C3—C4     | -0.6(5)            | C13—C14—C15—C16 | 0.5(5)             |
| C2—C3—C4—C5     | 0.8(5)             | C14—C15—C16—C17 | -1.0(6)            |
| C3—C4—C5—C6     | -0.7(5)            | C13—C12—C17—C16 | 0.7(4)             |
| C2—C1—C6—C5     | -0.2(4)            | O6—C12—C17—C16  | 178.4(3)           |
| O2—C1—C6—C5     | 178.8(3)           | C15—C16—C17—C12 | 0.4(5)             |

Selected bond lengths were illustrated in Table 3. The bond length of P (1)-O (1) is 1.4410(17) Å, which is close to those of P=O double bond of other phosphates (0.1452 nm). The bond length of P (1)-O (2) outside the ring is 1.5763(17) Å, and the bond lengths of P (1)-O (3) and P (1)-O (4) inside the ring are 1.5608(17) Å and 1.5698(18) Å, respectively. The six average bond lengths of P-O in the crystal structure is 0.1569(3) nm, which nearly equals to the 0.1571(1) nm and 0.1575(4) nm. The bond length of P-O bond outside the ring is observed to be shorter than that of inside the ring. It is due to the tension in the ring is acting. Similarly, the bond length of C(1)-O(2) outside the ring is 1.416(3) Å, the bond lengths of O(3)-C(9) and O(4)-C(7) inside the ring are 1.449(3) Å and 1.447(3) Å, respectively. The six average bond lengths of C-O single bond in the crystal structure is nearly 0.1447(5) nm, which is close to 0.1454(3) nm. The two average bond lengths of C-O bond outside the ring are longer than that of inside the ring, which also because the tension in the ring is acting. The four average bond lengths of C-C bond of the non-phenyl are 1.5273 Å, which equals to 0.15202nm [20]. The C(8) atom connected with two six-atom rings adopts sp3 hybrid orbit, the angles of C(7)-C(8)-C(9), C(7)-C(8)-C(10), C(10)-C(8)-C(11), C(9)-C(8)-C(11), C(7)-C(8)-C(11) and...
C(9)-C(8)-C(10) are 109.53°, 107.73°, 108.99°, 112.47°, 108.90° and 109.10°, respectively. All of the angles approach to the criterion tetrahedron (109°28′). As a result, the C(7), C(9), C(10) and C(11) linked to C(8) atom form slight distortion tetrahedron.

Table 3 Bond lengths for the SPEPA.

| Bond     | Bond length(Å) | Bond     | Bond length(Å) | Bond     | Bond length(Å) |
|----------|----------------|----------|----------------|----------|----------------|
| P(1)-O(1) | 1.4410(17)     | C(2)-C(3) | 1.384(4)      | C(9)-H(9B) | 0.9700        |
| P(1)-O(3) | 1.5608(17)     | C(2)-H(2A) | 0.9300         | C(10)-H(10A) | 0.9700        |
| P(1)-O(4) | 1.5698(18)     | C(3)-C(4) | 1.361(5)      | C(10)-H(10B) | 0.9700        |
| P(1)-O(2) | 1.5763(17)     | C(3)-H(3A) | 0.9300         | C(11)-H(11A) | 0.9700        |
| P(2)-O(5) | 1.4465(19)     | C(4)-C(5) | 1.362(5)      | C(11)-H(11B) | 0.9700        |
| P(2)-O(8) | 1.5525(17)     | C(4)-H(4A) | 0.9300         | C(12)-C(13) | 1.364(4)      |
| P(2)-O(7) | 1.5716(18)     | C(5)-C(6) | 1.384(5)      | C(12)-C(17) | 1.372(4)      |
| P(2)-O(6) | 1.5844(18)     | C(5)-H(5A) | 0.9300         | C(13)-C(14) | 1.387(5)      |
| O(2)-C(1) | 1.416(3)       | C(6)-H(6A) | 0.9300         | C(13)-H(13A) | 0.9300        |
| O(3)-C(9) | 1.449(3)       | C(7)-C(8) | 1.535(3)      | C(14)-C(15) | 1.380(6)      |
| O(4)-C(7) | 1.447(3)       | C(7)-H(7A) | 0.9700         | C(14)-H(14A) | 0.9300        |
| O(6)-C(12) | 1.411(3)      | C(7)-H(7B) | 0.9700         | C(15)-C(16) | 1.359(6)      |
| O(7)-C(10) | 1.454(3)      | C(8)-C(11) | 1.520(3)      | C(15)-H(15A) | 0.9300        |
| O(8)-C(11) | 1.461(3)      | C(8)-C(9) | 1.525(3)      | C(16)-C(17) | 1.383(5)      |
| C(1)-C(2) | 1.364(4)       | C(8)-C(10) | 1.528(3)      | C(16)-H(16A) | 0.9300        |
| C(1)-C(6) | 1.371(3)       | C(9)-H(9A) | 0.9700         | C(17)-H(17A) | 0.9300        |

4. Conclusion
Spirocyclic pentaerythritol phenol ester of phosphoric acid (SPEPA) as a kind of intumescent flame retardant has been synthesized for several years. In this paper, the crystal diffraction of SPEPA was studied. The crystal structures belong to orthorhombic, Pna2₁ space group and the two six-membered rings linked to the same atom C(8) belongs to chair conformations, which were vertical to each other to form stable spiro structure and an irregular axisymmetric structure in the space. It is the reason that phenol ester has good fire resistance.

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