# Inclusion property and Diels-Alder reaction of bis (diphenyl-phosphine oxide) butadiyne

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The host molecule, bis (diphenylphosphine oxide) butadiyne (2), includes a variety of guests to form five complexes (2a—2e). In addition, the Diels-Alder reaction between 2 and anthracene gives 9, 9', 10, 10'-tetrahedron-9, 9', 10, 10'-biethenoantracene-11, 11'-bis (diphenylphosphine oxide) (3) which is a potential di- $\pi$ -methane reactant and can undergo photorearrangement.

**Keyword** Inclusion, Diels-Alder reaction, phosphine oxide, solid-state reaction

## Introduction

1,1,6,6-Tetraphenylhexa-2,4-diyne-1,6-diol (1)

has the property of including a variety of organic compounds to form crystalline complexes<sup>1</sup> and has been widely used as separating and resoluting reagent, which provide a new route to extract active components from traditional Chinese medicine.<sup>2</sup> Its inclusion property is mainly related to its rigid structure of diacetylene linkage and its bulky shape.

Triphenylphosphine oxide (TPPO) is a good proton acceptor, and has been known to form complexes in solution with a variety of organic molecules.<sup>3-5</sup> These complexes are stabilized by the strong hydrogen bonds between the phosphoryl oxygen and the proton donors of the substrates.<sup>6</sup>

Compound 2: host; Compounds a - e: guest

Our model compound bis (diphenylphosphine oxide) butadiyne (2) has both characters of 1 and TPPO, and can been easily modified into P-chiral molecule.

Moreover, compound 2 undergoes Diels-Alder reaction with anthracene to give a new compound 9,9',10,10'-tetrahedron-9,9',10,10'-biethenoantracene-11,11'-bis-

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(diphenylphosphine oxide) (3). Compound 3 is a novel host molecule and can undergo an enantioselective photorearrangement as a potential di- $\pi$ -methane reactant.<sup>7,8</sup> In this work, we report the inclusion property of 2 and Diels-Alder reaction of 2 with anthracene in the solid state.

### Result and discussion

Synthesis of the host 29-12

Two methods have been reported to synthesize 2 according to Refs. 11 and 12. The first one gives 2 in poor yield and the second requires a precursor which is difficult to obtain. We choose the first one for its available starting material and improved it (Scheme 1). In the preparation of intermediate 4, we introduced excessive diacetylene at  $5^{\circ}$ C and diluted Ph<sub>2</sub>PCl with THF. As a result, the yield of 4 rises from 26% to 50%. In the preparation of 2, we used acetone as solvent instead of H<sub>2</sub>O and the yield rose from 40% to 80%.

#### Scheme 1

# Inclusion property of 2

The complexes of 2 were characterized by <sup>1</sup>H NMR, elemental analysis and solid-state IR. <sup>1</sup>H NMR and elemental analysis gave the stoichiometry of guest to

host. IR spectra showed that O—H and N—H peaks of the complexes shifted to lower frequency. The melting point showed that mp of the complexes was sharper than that of the mixture of 2 and the guests.

Table 1 Melting points of the complexes of 2 with various guests<sup>a</sup>

Guest	Medium	Guest mp (℃)	Complexes $(2a-2e)$ mp $(\mathcal{C})$	Ratio of Host: Guest
a	CH <sub>2</sub> Cl <sub>2</sub> / petroleum ether	122—127	156—158	1:2
b	CH <sub>2</sub> Cl <sub>2</sub> / petroleum ether	95—96	140—141	1:2
c	CH <sub>2</sub> Cl <sub>2</sub> //MeOH/ petroleum ether	171—174	165	1:2
d	CH <sub>2</sub> Cl <sub>2</sub> / petroleum ether	106—108	136—137	1:2
e	CH <sub>2</sub> Cl <sub>2</sub> //MeOH/ petroleum ether	126	104—105	1:1

<sup>&</sup>lt;sup>a</sup> Compound 2: mp = 192 °C.

Diels-Alder reaction between 2 and anthracene

Compound 3 was synthesized according to Scheme 2, which appeared to be flexible enough to allow vari-

able substitution at 9, 10-anthracene. The Diels-Alder reaction was carried out in solid state. After recrystal-lized from CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether, 3 was characterized by IR, <sup>1</sup>H NMR, MS, and elemental analysis.

#### Scheme 2

In IR spectrum, the  $\nu(C \equiv C)$  characteristic absorption (2096 cm<sup>-1</sup>, strong) of 2 disappeared in 3. The <sup>1</sup>H NMR spectrum showed the expected bridge H. The molecular ion (m/z 806) of 3 was observed under EI conditions and further characteristic fragments were formed by loss of reasonable fragments from this ion. The elemental analysis showed the expected results. Compound 3 gave well-formed crystals, and X-ray structure determination is in progress.

# **Experimental**

Melting points were determined with microscope melting point apparatus and uncorrected. <sup>1</sup>H NMR spectra were recorded on a Jeol FX-90 Q or Bruker AC-P 200 in CDCl<sub>3</sub>. Elemental analysis was carried out by YANA-CO CHN CORDER MT-3 apparatus. IR spectra were recorded on a PYE UNICAN SP-300 and mass spectra on a VG-70 spectrometer. Solvents were dried and distilled before use. Tetrahydrofuran (THF) was dried over sodium benzopheneone. Ph<sub>2</sub>PCl was purchased from Aldrich.

# Bis (diphenylphosphine) butadiyne (4)

The apparatus for preparing bis (diphenylphosphine) butadiyne consisted of a decomposition flask (A) and a reactor flask (B). The diacetylene was generated by adding 1,4-dichloro-2-butyne (5.07 g, 0.042 mol), potassium hydroxide (5.55 g, 0.10 mol), water (45 mL) and dioxane (4.5 mL) to flask A and the mixture was stirred vigorously under reflux. The diacetylene was then led into a previously prepared solution of ethylmagnesium bromide (magnesium 0.066 mol; EtBr, 0.066 mol; THF, 60 mL) at  $-5\,^{\circ}\text{C}$  in flask B. The solution was cooled to  $-10\,^{\circ}\text{C}$  and to which Ph<sub>2</sub>PCl (14.56 g,

0.066 mol) in 100 mL THF was added dropwise. The mixture was stirred at room temperature for 2 h, hydrolyzed with a saturated solution of NH<sub>4</sub>Cl and extracted with pentane ( $3 \times 100$  mL). The pentane layer was dried over anhydrous magnesium sulfate and evaporated to give a greenish residue. <sup>12</sup> The residue was washed with boiling MeOH to give 4 as pale beige powder, yield 50% (Lit. <sup>12</sup> 42%, Lit. <sup>11</sup> 26%), mp 105 °C.

# Bis (diphenylphosphine-oxide) butadiyne (2)

 $H_2O_2$  in acetone (3%, 12 mL) was dropped into a solution of **4** (1.5 g, 3.6 mmol) in acetone (13 mL), and was refluxed for half an hour, then the solvent was removed to leave a solid, which was recrystallized from MeOH to give **2**, as colorless crystals, 1.3 g, yield 80%. mp 192°C (Lit. <sup>15</sup> 191°C).  $\nu_{max}$ : 2096( $C \equiv C$ ), 1598, 1210, 1180, 1120, 1100 cm<sup>-1</sup>,  $\delta_H$ : 7.2—7.8 (m, ArH), m/z(%): 450(M<sup>+</sup>); 373(M<sup>+</sup> – Ph<sub>2</sub>P = O); 225(M<sup>+</sup>/2), 201(Ph<sub>2</sub>P = O<sup>+</sup>). Anal.  $C_{28}H_{20}$ -P<sub>2</sub>O<sub>2</sub>. Calcd: C,74.66; H,4.48. Found: C,74.51; H, 4.59.

### Complexes of 2

Complexes of **2** were prepared by dissolving 0.1 mmol of guests (**a**—**f**) and 0.05 mmol of **2** together in solution in the ratio listed in Table 1, then allowing the solution to evaporate slowly at room temperature.

2a  $\nu_{\text{max}}$ : 3120(OH) (a, 3300), 2100(C  $\equiv$  C), 1652, 1559, 1440, 1398, 1250, 1220, 1100, 1080 cm<sup>-1</sup>.  $\delta_{\text{H}}$ : 7.2—7.8(m, 34H, ArH) 6.5(s, 2H, OH). Anal. Calcd: C, 78.04; H, 4.91. Found: C, 77.82; H, 4.97.

2b  $\nu_{max}$ : 3170—3020(OH)(b, 3300), 2100 (C  $\equiv$  C), 1573, 1435, 1380, 1365, 1278, 1210, 1195, 1160, 1120, 1100, 1080 cm<sup>-1</sup>.  $\delta_{H}$ : 7.2—7.8 (m, 27H, ArH); 6.8—6.9(dd, 1H, OH). Anal. Calcd: C, 78.04; H, 4.91. Found: C, 77.94; H, 5.37.

2c  $\nu_{max}$ : 3200 (OH) (c, 3220), 2100 (C  $\equiv$  C), 1590, 1510, 1470, 1440, 1250, 1220, 1180, 1120, 1000, 830 cm<sup>-1</sup>.  $\delta_{H}$ : 7.2—7.8 (m, 48H, ArH); 2.7—5.0(m, 4H, OH). Anal. Calcd: C, 71.64; H, 4.81. Found: C, 71.58, H, 4.62.

2d  $\nu_{max}$ : 3447, 3315(NH)(d, 3415, 3325), 2100(C $\equiv$ C), 1640, 1505, 1435, 1290, 1210, 1298, 1115, 1098 cm<sup>-1</sup>.  $\delta_{H}$ : 7.2 $\longrightarrow$ 7.8(m, 48H, ArH); 6.8 (s, 2H, NH). Anal. Calcd: C, 78.25; H, 5.20; N, 3.80. Found: C, 78.30; H, 5.16; N, 4.06.

2e  $\nu_{max}$ : 3260—3200(OH)(e, 3350—3230), 2980, 2940, 2100(C $\equiv$ C), 1440, 1210, 1170, 1120, 1100, 945 cm<sup>-1</sup>.  $\delta_{H}$ : 7.2—7.8(m, 20H, ArH); 1.2—1.5(m, 12H, CH). Anal. Calcd: C, 74.02; H, 5.56. Found: C, 73.92; H, 5.82.

9,9',10,10'-Tetrahedron-9,9',10,10'-biethenoantracene-11,11'-bis (diphenylphosphine oxide) (3)

Compound 3 was prepared by heating the powder mixture of 2 (0.2678 g, 0.59 mmol) and anthracene (0.3152 g, 1.77 mmol) up to 220°C and the melted mixture was kept at 200°C for about 30 min until it solidified again. The excessive anthracene was sublimed after reaction. Recrystalized from CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether, 3-CH<sub>2</sub>Cl<sub>2</sub> was obtained as colorless crystals, yield 94%, mp > 300°C.  $\nu_{max}$ : 3390 (OH), 3052

(CH), 2960, 1630, 1590, 1460, 1437, 1262, 1250, 1205, 1160, 1120, 1100, 1160 cm<sup>-1</sup>,  $\delta_{\rm H}$ : 7.2—7.8 (m, 36H, ArH); 4.76—4.98 (m, 4H, bridgehead H). m/z(%): 806(M<sup>+</sup>, 0.12); 605(M<sup>+</sup> - Ph<sub>2</sub>P = 0, 8.29); 201(O = PPh<sub>2</sub><sup>+</sup>, 13.57); 178(C<sub>14</sub>H<sub>10</sub><sup>+</sup>, 100). Anal. C<sub>56</sub>H<sub>40</sub>P<sub>2</sub>O<sub>2</sub>/CH<sub>2</sub>Cl<sub>2</sub>: Calcd: C, 76.77; H, 4.75. Found: C, 77.09; H, 4.88.

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