

# 단 신

## 1,8-무수나프탈렌과 다이아민을 사용하여 일차원적 다이이미드형성에 관한 연구: Rigid Space에 Central Hub의 일차원적 연결

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## The Study of One Dimensional Diimide Formation from 1,8-Naphthalic Anhydride and Diamines: Linear Connection of "HUB" with Rigid Spacer "Spoke"

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Attachment of spoke to hubs remains a critical issue<sup>1</sup> and we pursued this goal with the naphthyl anhydride spoke **2** and various amine-bearing hubs **1** in the reaction conditions (Fig. 1).

The exploration of model system chemistry has helped us to identify high yielding spoke-hub connection reaction. Six-membered ring anhydride **2** is more stable and its reactivity towards an amine group is lower than its five-membered analogues.<sup>1c</sup> Hence it is necessary to use a catalyst in the reactions of such anhydrides with diamines to prepare the complete hub-spoke-connector monomers. We reported that zinc acetate was the most effective catalyst for the preparing of diimide and triimide from 1,4-phenylenediamine and 1,3,5-phenylenetriamine, respectively, in good yields.<sup>2</sup>

We continued to study the connection of spoke with different hub units such as 1,4-diacetyl benzene, ethane, or cyclohexane. At first, we tried to connect 1,8-naphthalic anhydride (**2**), the spoke to the diacetylenebenzene **6** as a hub unit. The iodoimide **5** was prepared from 1,8-naphthalic anhydride (**2**) and 4-iodoaniline (**4**) in the

presence of a catalytic amount (10 mol %) of  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  in quinoline at 200°C.<sup>2</sup> In this reaction, the iodoimide **5** was formed in 98% yield (Scheme 1). Diimide **7** as hub-spoke connector was obtained in 76% yield from the iodoimide **5** and 1,4-diacetylenebenzene (**6**) in the presence of  $\text{PdCl}_2$ , triphenylphosphine, and  $\text{CuI}$  at 50 °C.<sup>3</sup>

Alternatively, we tried to connect 1,8-naphthalic anhydride (**2**) to the 1,2-diaminoethane **8**, hub. We expect the hub and spoke to be connected in linear fashion as shown in the newman projection (Scheme 2). The diimide **9** was prepared from 1,8-naphthalic anhydride (**2**) and 1,2-diaminoethane (**8**) in DMAC at 165°C. In this reaction, the diimide **9** was formed in 83% yield. Also, we tried to use *trans*-1,4 diaminocyclohexane as a hub unit. Both amino groups are positioned equatorial. The diimide **11** was thus prepared from 1,8-naphthalic anhy-

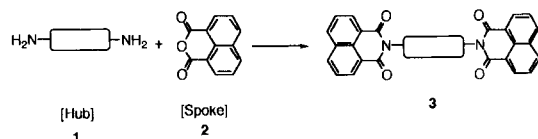
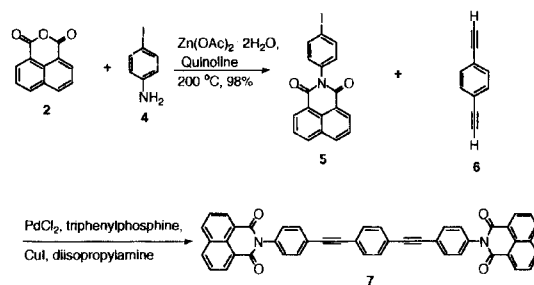
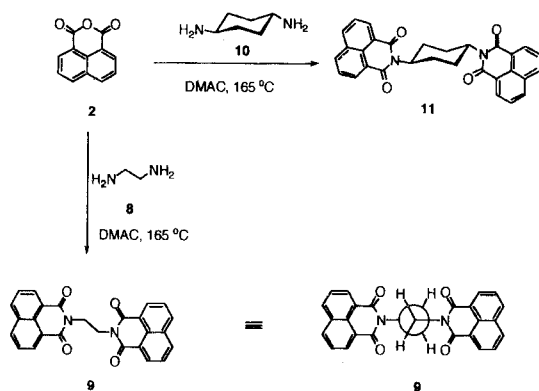


Fig. 1. Hub-Spoke Connection.



Scheme 1.



Scheme 2.

dride (2) and *trans*-1,4 diaminocyclohexane (10) in DMAC at 165°C. The diimide 11 was formed 89% yield and insoluble in most organic solvents. We will continue search the soluble organic solvents. Diimide 11 was characterized by infrared spectroscopy and mass spectroscopy.

## Experimental

**General.** All commercial chemicals were used as obtained without further purification, and all solvents were carefully dried and distilled by standard methods prior to use. Column chromatography was carried out on silica gel 60 (E. Merck, 230~400 mesh) with the flash technique.<sup>4</sup> Nuclear magnetic resonance spectra were recorded on either WP-200 or AM-300 spectrometer. Chemical shifts are reported in ppm relative to  $(\text{CH}_3)_4\text{Si}$  for  $^1\text{H}$  NMR. Coupling constants (*J*) are reported in Hz. Infrared spectra ( $\text{cm}^{-1}$ ) were obtained on a Perkin-Elmer 1600 FT infrared spectrometer. Positive fast atom bombardment mass spectra (FABMS) were obtained in a 2-nitrophenylether matrix. Combustion analyses were performed by Midwest Microlabs, Indianapolis, IN, USA.

**Iodo imide 5.** A mixture of 1,8-naphthalic anhydride (2) (0.349 g, 1.76 mmol), 4-iodo aniline (4) (0.386 g, 1.76 mmol), and  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (0.386 g, 1.76 mmol) was heated in quinoline for 2 hrs at 200. The solution was cooled to room temperature, diluted with 200 mL of  $\text{CH}_2\text{Cl}_2$  and washed with 1.0 M HCl (2×100 mL) and brine (100 mL). The organic layer was dried over  $\text{Na}_2\text{SO}_4$  and concentrated by rotary evaporation to a yellow solid.

low solid. Column chromatography on silica gel (100%  $\text{CH}_2\text{Cl}_2$ ) separated desired iodoimide 5 as a light yellow solid (0.693 g, 98). mp 278-281; IR ( $\text{CHCl}_3$ )  $\text{cm}^{-1}$  1713 (s), 1670 (s), 1588 (m), 1485 (m);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 7.06 (d, *J*=8.5, 2H), 7.77 (dd, *J*=7.3, 8.5, 2H), 7.85 (d, *J*=8.5, 2H), 8.26 (dd, *J*=0.7, 8.3, 2H), 8.62 (dd, *J*=0.7, 7.3, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) 122.5, 127.2, 130.7, 131.4, 131.5, 134.4, 135.9, 137.7, 163.5; mass spectrum *m/z* (relative intensity) 399 ( $\text{M}^+$ , 100), 180 (46), 126 (20); *Anal. calcd* for  $\text{C}_{18}\text{H}_{10}\text{INO}_2$ : C, 54.16; H, 2.53; found: C, 55.41; H, 2.77.

**Diimide 7.** To the mixture of  $\text{PdCl}_2$  (2 mg, 0.01 mmol), triphenylphosphine (3 mg, 0.01 mmol), and  $\text{CuI}$  (4 mg, 0.02 mmol) was added the solution of iodoimide (5) (82 mg, 0.21 mmol) and 1,4-diacetylenebenzene (6) (14 mg, 0.11 mmol) in 5 mL of diisopropylamine. The reaction mixture was stirred at 50 for 2 hrs. The reaction mixture was cooled down to room temperature and quenched with 1M  $\text{CuSO}_4$ . The reaction mixture was diluted with  $\text{CH}_2\text{Cl}_2$  (200 mL), washed with  $\text{H}_2\text{O}$  (2×150 mL), and brine (150 mL). The organic layer was dried over  $\text{Na}_2\text{SO}_4$ , filtered and concentrated in vacuo. Purification of the crude light yellow solid with flash chromatography gave 100 mg (76%) of pure diimide 7. IR ( $\text{CHCl}_3$ )  $\text{cm}^{-1}$  1709 (s), 1668 (s), 1589 (s), 1374 (s);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) 7.33 (d, *J*=8.5, 4H), 7.56 (s, 4H), 7.71 (d, *J*=8.5, 4H), 7.82 (dd, *J*=7.1, 8.3, 4H), 8.29 (dd, *J*=0.9, 8.8, 4H), 8.66 (dd, *J*=0.9, 7.1, 4H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) 89.7, 90.7, 122.7, 123.1, 123.7, 127.1, 128.5, 128.9, 133.7, 131.7, 132.6, 134.4, 135.4, 164.2; MS (FAB $^+$ ) *m/z* 669 ( $\text{M}^+$ +1).

**Naphthalic diimide 9.** The flask was charged with 1,8-naphthalic anhydride (2) (0.19 g, 0.97 mmol), ethylenediamine (8) (0.029 g, 0.49 mmol), and 10 mL of DMAC. The solution was stirred at 165 for 20 hrs and then cooled to room temperature to get insoluble solid. Upon washing with hexane (2×100 mL) and ethyl acetate (2×100 mL), 0.17 g of the pure naphthalic diimide 9 was obtained as a yellow solid (83%). mp 312~316; IR (KBr)  $\text{cm}^{-1}$  1709, 1664;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) 4.64 (s, 4H), 7.65 (dd, *J*=7.3, 8.7, 4H), 8.16 (dd, *J*=0.8, 8.3, 4H), 8.43 (dd, *J*=0.8, 7.3, 4H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) 39.1, 122.6, 126.8, 128.3, 131.2, 131.6, 133.8, 164.6; mass spectrum *m/z* (relative intensity) 420 ( $\text{M}^+$ , 44.5), 223 (100), 222 (60), 210 (40).

**Naphthalic diimide 11.** To a flask charged with 1,8-naphthalic anhydride (**2**) (0.79 g, 3.99 mmol) and cyclohexyldiamine (**10**) (0.23 g, 2.02 mmol) was added 10 mL of DMAC. The solution was stirred at 165 for 2 hrs and then cooled to room temperature to get insoluble solid. Simple washing with hexane (2×100 mL), gave 0.85 g of the pure naphthalic diimide **11** as a gray solid (89%), mp >340; IR (KBr)  $\text{cm}^{-1}$  1694 (s), 1654 (s), 1627 (s), 1585 (s); mass spectrum  $m/z$  (relative intensity) 474 ( $M^+$ , 13), 277 (15), 198 (100), 44 (69).

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