

## 5,11-Dihydro-5,11-di-1-naphthylindolo[3,2-*b*]carbazole: Atropisomerism in a Novel Hole-Transport Molecule for Organic Light-Emitting Diodes

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The search for new hole-transport molecules forming stable amorphous films has been motivated by the application of such materials in organic light-emitting diodes (LEDs).<sup>1–8</sup> Typically, organic LEDs based on small organic molecules are constructed on an ITO (indium tin oxide) anode by vacuum deposition, with an organic hole-transport layer and a tris(8-hydroxyquinoline)-aluminum (Alq<sub>3</sub>) electron-transport layer that also serves as a light emitter. The device is capped with a magnesium–silver alloy which serves as a cathode. The primary role of the hole-transport layer is to assist hole injection from the anode into the light-emitting layer and to block electrons within this layer, thus maximizing the recombination probability of the injected carriers. The materials used in this layer must be good hole conductors and have a small energy barrier for hole injection from the anode. Hole-transport molecules used in organic LED devices are usually based on the triarylamine functionality, such as *N,N'*-diphenyl-*N,N'*-di-*m*-tolyl-1,1'-biphenyl-4,4'-diamine (TPD), *N,N'*-di-1-naphthyl-*N,N'*-diphenyl-1,1'-biphenyl-4,4'-diamine (NPD), and related equivalents. Although triarylamine compounds exhibit excellent hole-transport properties, they generally produce amorphous films with poor morphological stability because of their low glass transition temperatures ( $T_g$ ); for example TPD has a  $T_g$  of 65 °C.<sup>3</sup> Previous studies have shown that one of the degradation modes in organic LED devices is ascribed to the thermal instability of the hole-transport layers made of such low  $T_g$  molecules.<sup>9</sup> Therefore, apart from their electronic properties, hole-transport molecules exhibiting high  $T_g$ 's are required for the construction

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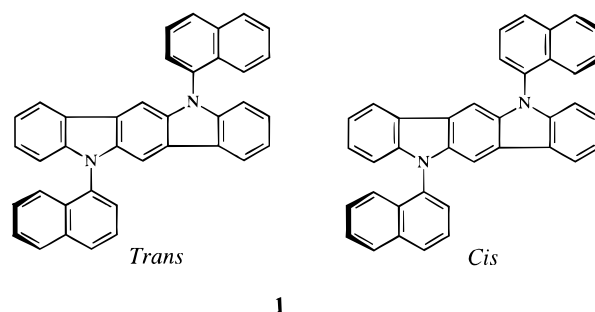


Figure 1. The molecular structures of **1**.

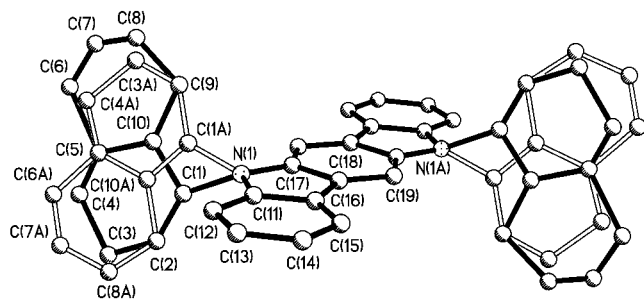
of long life devices. A variety of approaches has been successfully adopted to the design of hole-transport molecules with high glass transition temperatures predominantly based on the triarylamine functionality, including starburst-shape amines,<sup>4</sup> spiro-linked amines,<sup>5</sup> oligomeric amines,<sup>6</sup> and those with rigid groups.<sup>7,8</sup> In this paper, we report a novel indolo[3,2-*b*]carbazole compound, **1** (Figure 1), as the hole-transport material for organic LEDs. This compound not only offers desirable hole-transport properties and high  $T_g$ , but also displays an unusual atropisomerism, resulting in two discrete rotational isomers, trans and cis, whose existence makes **1** readily form a stable amorphous glass.

Compound **1** was prepared in about 60% yield from an Ullmann condensation reaction of 5,11-dihydroindolo[3,2-*b*]carbazole<sup>10</sup> with 1-iodonaphthalene. The reaction was carried out at 230 °C in tridecane in the presence of a catalytic amount of cupric sulfate and potassium carbonate as hydrogen iodide scavenger. It was purified through an alumina column using hot toluene as eluent, followed by train sublimation.<sup>11</sup> In solution, compound **1** was found to exist in two isomeric forms, trans and cis, attributable to the hindered rotation of the bond binding the naphthyl group, as confirmed by NMR studies.<sup>12</sup> The isomeric structures of **1** were further confirmed by a single-crystal X-ray diffraction analysis on crystals selected from the sublimed product.<sup>12</sup> As shown in Figure 2, the two naphthyl rings in compound **1** have two different orientations in the solid state which can be attributed to the coexistence of the trans and the cis isomers. The occupancy factors for the two sites were found to be approximately 0.50:0.50. Since the cis form is chiral, it contains two enantiomers, while the trans form is a mesomer. NMR analysis revealed that the trans and cis isomers exist in the sublimation product in an approximately equal amount, indicating that they have similar volatility. Although attempts to isolate one of the isomers by recrystallization from different solvents failed, an enriched mixture could be obtained from the first crop of the precipitates from a chlorobenzene solution of **1**. As monitored by NMR, no interconversion between the two isomers was observed in boiling chloroform for 3 h, or

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(12) Element analysis for **1**(1:1 isomer mixture): Calcd for C<sub>38</sub>H<sub>24</sub>N<sub>2</sub>: C, 89.74; H, 4.76; N, 5.51. Found: C, 89.69; H, 4.76; N, 5.56. NMR (CDCl<sub>3</sub>)  $\delta$ <sub>H</sub> 6.98 (d,  $J$  = 7.8 Hz, 2H), 7.17 (double t,  $J_1$  = 7.0 Hz,  $J_2$  = 0.9 Hz, 2H), 7.24–7.63 (m, 6H), 7.72 and 7.73 (two s, 2H), 7.74–7.78 (m, 4H), 8.02 (d,  $J$  = 7.8 Hz, 2H), 8.09 (d,  $J$  = 8.4 Hz, 2H), 8.12 (t,  $J$  = 5.0 Hz, 2H);  $\delta$ <sub>C</sub> 100.28 (100.31), 109.85 (109.89), 119.04, 120.27 (120.29), 123.22 (123.24), 123.26 (123.28), 123.73, 123.79, 125.92 (125.95), 126.13, 126.74, 127.00, 127.02 (127.06), 128.49, 128.91 (128.94), 131.20, 134.66 (134.71), 134.99 (135.00), 138.39, 143.30 (143.32). Crystal data for **1**:  $a$  = 10.072(2) Å,  $b$  = 11.099(2) Å,  $c$  = 12.915(2) Å,  $\beta$  = 112.007(4)°,  $V$  = 1338.6(4) Å<sup>3</sup>,  $Z$  = 2, monoclinic,  $P2_1/n$ . Data were collected over the  $2\theta$  range of 2.21–53.0° at 23 °C on a Siemens CCD X-ray diffractometer with Mo K $\alpha$  radiation. Data were processed on a pentium PC using Siemens SHELXTL software package (5.0). Convergence to the final  $R$  values of  $R_1$  = 0.0866,  $wR_2$  = 0.1934 ( $I$  > 2 $\sigma(I)$ ) and  $R_1$  = 0.1915,  $wR_2$  = 0.2385 (all data) for **1** were achieved by using 2752 reflections and 260 parameters. The details of X-ray crystallographic analyses are given in the Supporting Information.



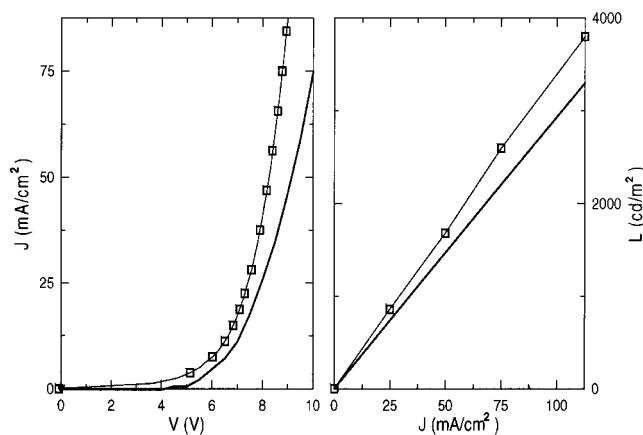
**Figure 2.** A diagram showing the crystal structure of **1** with labeling schemes. For clarity, all atoms are shown as ideal spheres, and hydrogen atoms are omitted. The second sets of naphthyl rings are shown by hollow bonds. Important bond lengths (Å) and angles (deg): N(1)–C(1A) 1.519(10), N(1)–C(1) 1.545(13), N(1)–C(17) 1.395(4), N(1)–C(11) 1.377(4), C(1)–N(1)–C(11) 115.5(4), C(1A)–N(1)–C(11) 128.3(3), C(1)–N(1)–C(17) 127.2(4), C(1A)–N(1)–C(17) 118.6(4), C(11)–N(1)–C(17) 109.0(3).

when the solid mixture was heated to 350 °C for 30 min, although it became a 1:1 mixture when it was melted at 390 °C. While atropisomerism in biaryl molecules is common,<sup>13</sup> to our knowledge, stable atropisomers resulting from the restricted rotation about the carbon–nitrogen bond are extremely rare.<sup>14</sup>

By virtue of their structural similarity, both trans and cis forms are anticipated to display identical electrochemical properties. Indeed, the cyclic voltammetry (CV) of **1** recorded only one redox wave which involves a single oxidation process followed by reduction with a half-wave oxidation potential ( $E_{1/2}$ ) of 0.93 V vs Ag/AgCl in  $\text{CH}_2\text{Cl}_2$ – $\text{Bu}_4\text{NClO}_4$  (0.1 M). The redox behavior is highly reversible; indicating that **1** possesses excellent electrochemical stability.

The amorphous nature of **1** is significant. Since it contains stereoisomers which impede crystallization in an amorphous state, **1** can readily form a stable glass. The thermal analysis by differential scanning calorimetry (DSC) showed that **1** survives a high melting point around 390 °C without decomposition. When the melt sample was cooled at 20 °C/min, it spontaneously formed an amorphous glass via a supercooled liquid state. A glass transition temperature at 164 °C was observed when the glassy sample was heated again at 20 °C/min. This amorphous state remained very stable at room temperature; no crystallization occurred even after standing for two months. Moreover, as evidenced by atomic force microscopy (AFM) **1** forms a stable uniform amorphous film by vacuum deposition.

Finally, the hole-transporting performance of **1** in organic LED devices was investigated. An OLED cell was constructed on an ITO substrate by sequential vacuum deposition of **1** as the hole-



**Figure 3.** The  $I$ – $V$  and  $L$ – $I$  characteristics of organic LED devices: device with **1** (□); device with NPD (—).

transport layer (750 Å),  $\text{Alq}_3$  as the electron-transport layer (800 Å), and Mg–Ag (10:1) alloy as cathode. When a positive bias was applied to the ITO, the device emitted a bright green light attributable to the intrinsic emission of  $\text{Alq}_3$ . The device performance characteristics were examined in comparison with a control device with an NPD hole-transport layer. As shown in Figure 3, The device with **1** displays a low threshold voltage and the current–voltage ( $I$ – $V$ ) characteristics similar to those of the NPD-based device, indicating that **1** functions as an excellent hole-transport layer. The luminance–current ( $L$ – $I$ ) plots also shows that similar EL efficiency (cd/A) can be achieved for the device with **1** as the hole-transport layer.

In summary, we have discovered a novel hole-transport molecule, **1**, which displays an unusual atropisomerism, resulting in two discrete rotational isomers with similar electronic properties. Due to the existence of these isomers **1** readily forms a stable amorphous glass with a high glass transition temperature of 164 °C, which is substantially higher than that of widely used NPD. Furthermore, **1** shows excellent hole-transport properties in organic LEDs, and its performance is practically equivalent to NPD. Given all of these attractive attributes, we expect that this new hole-transport material will find important device applications. The present discovery also represents a new strategy for the molecular design of amorphous materials by creating stereoisomers exhibiting identical electronic properties.

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**Supporting Information Available:**  $^1\text{H}$  NMR spectra of **1** (1:1 mixture) and of its enriched mixture treated at elevated temperatures, and tables of crystal data, atomic coordinates and isotropic thermal parameters, bond lengths and angles, anisotropic thermal parameters, and hydrogen parameters (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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