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Structural, spectral, electrochemistry, thermal properties and theoretical studies on 4-[N, N-di(4-tolyl)amino] benzaldehyde -2-chloro benzoylhydrazone

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HIGHLIGHTS

- 4-[N, N-di(4-tolyl)amino] benzaldehyde-2-chloro benzoylhydrazone were synthesized and characterized.
- The photophysical, thermostability properties of the titled compound were found to be distinctively modified by benzoylhydrazone structure.
- DFT calculations and experimental results were coincided on structure, energy gap and electrochemistry.
- The hydrogen bonding interactions within sheets and π–π interactions 3D network confirmed the title compound can be used as amorphous material in nonpolar solvents.

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ABSTRACT

The title compound 4-[N, N-di(4-tolyl)amino] benzaldehyde-2-chloro benzoylhydrazone ($C_{28}H_{24}ClN_3O$, M_r = 453.96) was synthesized by the reaction of 4-[N, N-di(4-tolyl)amino] benzaldehyde with 2-chlorobenzohydrazide, and its structure was characterized by IR, ^{1}H NMR, ^{13}H NMR, high-resolution mass spectrometry and single-crystal X-ray diffraction. The crystal belongs to Monoclinic, space group *P2(1)/n* with *a* = 12.626(3), *b* = 12.609(3), *c* = 15.837(3) Å, *β* = 90.00(3)°, *Z* = 5, *V* = 2512.5(9) Å^3, M_r = 453.95, *Dc* = 1.280 g/cm^3, *μ* = 0.183 mm^{-1}, *F*(000) = 1024, *R* = 0.0432 and *wR* = 0.1087. X-ray analysis revealed that one of the benzene ring and acylhydrazone were essentially planar, the 2-chloro benzene ring and amide were non-planar, the torsion angles C(1)—C(6)—C(7)—O(1) and C(5)—C(6)—C(7)—O(1) are 61.4(5)° and −114.4(4)°. The thermal stability studies indicate that the title compound is stable up to 341.1 °C. The spectral, electrochemistry properties and theoretical studies show that the title compound is a good candidate for the charge-transporting materials.

Introduction

In the process of the large-scale manufacturing of the opto devices, amorphous molecular materials used as hole-transport materials must be capable of forming uniform amorphous thin films by either vacuum deposition or spin coating from solution. Triphenylamine-based hydrazones used as organic hole-transport materials have been widely studied [1–6]. Up to now, the efforts have been laid on developing solution processable organic small molecules, for that they offer the advantages of simple preparation/purification procedures, lower cost and the high reproducibility in the performance of the device. The recent extensive studies have revealed that small triphenylamine-based molecules can also form stable amorphous glasses above room temperature if their molecular structures are properly designed [7–9]. The following strategies have been adopted for this purpose [1]: (1) Molecules should possess nonplanar molecular structures; (2) The incorporation of bulky and heavy substituents leads to enhanced stability of the resulting amorphous glasses; (3) The introduction of structurally rigid moieties can increase the thermal stability. In our concept, we designed the triphenylamine-based hydrazones which the enlarged system of conjugated π-electrons of the target molecular would reinforce the inclination of the molecules to form glasses and would allow enhanced charge-carrier mobilities. On the other hand, the presence of hydrazide and cholro

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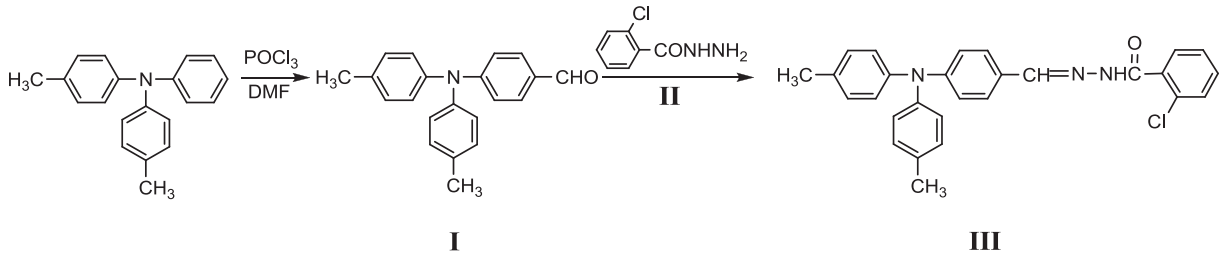

Scheme 1. Synthesis route of the compound **III**.

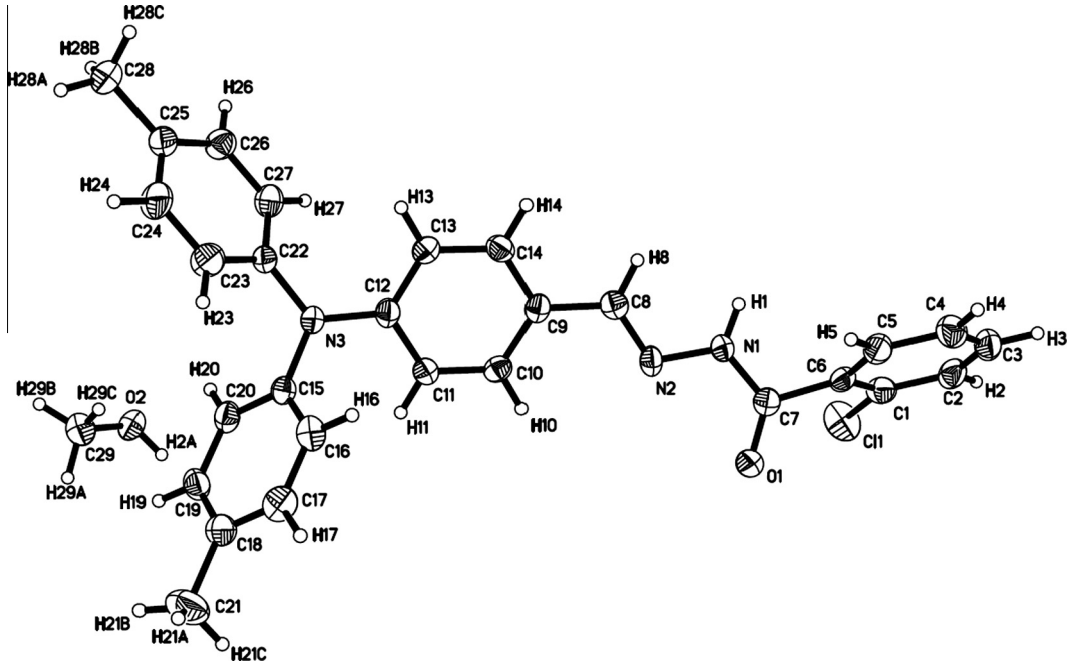

Fig. 1. Molecular structure of the compound **III**.

Table 1
Selected optimized and experimental geometries parameters of the title compound in ground state.

Bond lengths (Å)	Exp./cal.	Bond lengths (Å)	Exp./cal.	Bond lengths (Å)	Exp./cal.
Cl(1)—C(1)	1.737(3)/1.772	C(1)—C(2)	1.391(5)/1.396	C(10)—H(10)	0.9500/1.088
O(1)—C(7)	1.228(4)/1.220	C(1)—C(6)	1.392(5)/1.404	C(11)—C(12)	1.404(4)/1.406
N(1)—C(7)	1.354(4)/1.377	C(2)—C(3)	1.372(5)/1.392	C(15)—C(16)	1.387(5)/1.403
N(1)—N(2)	1.393(3)/1.361	C(2)—H(2)	0.9500/1.085	C(16)—C(17)	1.387(5)/1.392
N(1)—H(1)	0.901(10)/1.017	C(6)—C(7)	1.510(5)/1.516	C(16)—H(16)	0.9500/1.086
N(2)—C(8)	1.289(4)/1.287	C(8)—C(9)	1.448(4)/1.458	C(17)—C(18)	1.391(5)/1.401
N(3)—C(12)	1.406(4)/1.411	C(8)—H(8)	0.9500/1.100	C(18)—C(21)	1.507(5)/1.511
N(3)—C(22)	1.425(4)/1.425	C(9)—C(10)	1.405(4)/1.404	C(21)—H(21A)	0.9800/1.095
N(3)—C(15)	1.439(4)/1.425	C(10)—C(11)	1.376(4)/1.389		
Angle (°)	Exp./cal.	Angle (°)	Exp./cal.	Angle (°)	Exp./cal.
C(7)—N(1)—N(2)	119.5(3)/119.2	C(12)—N(3)—C(15)	118.2(3)/120.5	O(1)—C(7)—N(1)	125.5(3)/123.4
C(7)—N(1)—H(1)	122(2)/120.0	C(22)—N(3)—C(15)	116.9(2)/119.1	O(1)—C(7)—C(6)	121.6(3)/120.5
N(2)—N(1)—H(1)	118(2)/119.2	C(2)—C(1)—Cl(1)	118.7(3)/115.9	N(2)—C(8)—C(9)	121.7(3)/122.1
C(8)—N(2)—N(1)	113.9(3)/116.6	C(6)—C(5)—H(5)	119.7/117.0	N(2)—C(8)—H(8)	119.2/121.3
C(12)—N(3)—C(22)	123.2(3)/120.4	C(1)—C(6)—C(7)	122.7(3)/128.8		
Torsion angle (Å)	Exp./cal.	Torsion angle (Å)	Exp./cal.	Torsion angle (Å)	Exp./cal.
C(7)—N(1)—N(2)—C(8)	177.9(3)/179.6	N(1)—N(2)—C(8)—C(9)	−178.8(3)/−179.9	C(12)—N(3)—C(15)—C(20)	−130.3(3)/−135.7
Cl(1)—C(1)—C(6)—C(7)	7.1(4)/8.9	N(2)—C(8)—C(9)—C(10)	−14.6(5)/−0.41	C(22)—N(3)—C(15)—C(20)	64.3(4)/65.1
N(2)—N(1)—C(7)—O(1)	2.9(5)/3.9	C(8)—C(9)—C(10)—C(11)	177.9(3)/179.6	C(12)—N(3)—C(15)—C(16)	51.3(4)/45.6
N(2)—N(1)—C(7)—C(6)	−172.6(3)/−179.6	C(22)—N(3)—C(12)—C(13)	16.5(5)/34.0	C(22)—N(3)—C(15)—C(16)	−114.1(3)/−115.2
C(1)—C(6)—C(7)—O(1)	61.4(5)/31.0	C(15)—N(3)—C(12)—C(13)	−147.9(3)/−145.1	C(5)—C(6)—C(7)—O(1)	−114.4(4)/−116.7

Exp./cal. = experimental/calculated.