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ScienceDirect
Journal of Molecular Structure 829 (2007) 202–207
Journal of MOLECULAR STRUCTURE
www.elsevier.com/locate/molstruc

Synthesis, crystal structures, and optical properties of a novel imidazole derivative and its Zn(II) complex

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Received 16 May 2006; received in revised form 24 June 2006; accepted 26 June 2006
Available online 22 August 2006

Abstract

A novel imidazole derivative, 1-[*trans*-4-(4-diethylaminostyryl)phenyl]imidazole (abbreviated as L), and its complex $Zn(SCN)_2L_2$ have been synthesized and fully characterized. Their crystal structures have been determined by X-ray diffraction. The molecular structure of L is approximately coplanar, the bond lengths of C–C and C–N are located between the normal double and single bonds, which show that L has a delocalized π-electron system in the molecule. In the molecular structure of $Zn(SCN)_2L_2$, zinc atom is four coordinated by two nitrogen atoms of the ligands (L) and two nitrogen atoms of thiocyanate to form a distorted tetrahedral geometry. The one-dimensional structure of $Zn(SCN)_2L_2$ is formed by C–H···S interactions and π–π interactions. They both crystallize in the noncentrosymmetric space group $P2_1$, and exhibit powder second-harmonic generation (SHG) efficiency approximately twenty times high as that of urea, indicating promising potential applications as useful nonlinear optical (NLO) materials.

Keywords: Imidazole; π-Conjugated system; SHG; Noncentrosymmetric

1. Introduction

There has been intensive research on organic, metal-organic materials exhibiting second-order nonlinear optical (NLO) properties [1]. Such materials are of potential applications in electrooptic devices and second harmonic generation (SHG), which are of importance in areas such as optical communications and data storage [2–4]. Two main factors determine the NLO response of molecules. The first important factor is the requirement of noncentrosymmetric arrangement of molecules in the crystal, because the second-order susceptibility (χ^2) will vanish in a centrosymmetric environment [5,6]. However, crystallization often rarely occurs in a noncentrosymmetric space group as design. It is not possible to predict crystal geometries from molecular geometries, which has greatly hampered the progress of crystal engineering of functional solids. Therefore, design and synthesis of acentric crystals have gained scientific and technological interest [7–11]. The second factor is the requirement of delocalized π-electron system of molecules. Accordingly, the rational design and synthesis of such acentric crystal with high SHG efficiency is still a challenge to synthetic chemists and material scientists.

Moreover, the organic–inorganic hybridized coordination complexes containing imidazole derivatives, which were designed based on topologies, have been extensively reported [12], but the π-conjugated imidazole derivatives with functional group and their metal complexes, which possess excellent optical properties, are relatively scarce. Therefore, we have systematically carried out research on

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doi:10.1016/j.molstruc.2006.06.025

the rational design and synthesis of noncentric imidazole derivatives and their complexes containing good electron donor (D) and acceptor (A) through a conjugated bridge, which is original and different from other related reports. In this article, we report the synthesis, crystal structures, thermal stabilities, photoluminescence and SHG efficiency of a novel D-π-A structural imidazole derivative (L) and its complex $Zn(SCN)_2L_2$ with noncentrosymmetric space group.

2. Experimental

2.1. General

All commercially available chemicals are of analytical grade and used without further purification. The solvents were purified by conventional methods. 4-(Diethylamino)benzaldehyde, 4-(diethylamino)benzalcohol, and [4-(diethylamino)benzyl]triphenylphosphinium iodide were synthesized according to the methods reported [13–15]. IR spectra were recorded on a Nicolet FT-IR instrument with KBr discs in the 400–4000 cm^{-1} range. Elemental analysis was carried out on Perkin-Elmer 240 analyzer. UV–vis spectra were measured in DMF solutions (10^{-5} mol L^{-1}) with a UV-265 spectrophotometer. The solid-state luminescence spectra were recorded on a Perkin-Elmer LS55B fluorescence spectrophotometer at room temperature.

2.2. Synthesis of 4-imidazolyl-benzaldehyde

DMF (60 mL), imidazole (6.80 g, 100 mmol), anhydrous potassium carbonate (13.80 g, 100 mmol), 4-fluorobenzaldehyde (12.40 g, 100 mmol) and three drops of aliquate-336 were added to a round-bottomed flask. The reaction mixture turned yellow and was kept stirring for 24 h at 85 °C. After being cooled to room temperature, it was poured into ice-water (200 mL). The pale-yellow lamellar crystals formed immediately. The product was filtered and dried in vacuo. Yield: 90%. Anal. calcd. (%) for $C_{10}H_8N_2O$: C, 63.58; H, 5.96; N, 9.27. Found (%): C, 63.55; H, 5.94; N, 9.26. MS: $m/z = 172$.

2.3. Synthesis of 1-[trans-4-(4-diethylaminostyryl)phenyl] imidazole (L)

[4-(Diethylamino)benzyl]triphenylphosphinium iodide (5.51 g, 10 mmol), 4-imidazolyl-benzaldehyde (1.72 g, 10 mmol) and NaOH (2.00 g, 50 mmol) were placed in a mortar. The mixture was ground for 10 min, then poured into distilled water (500 mL). The product was extracted twice with CH_2Cl_2, and the organic layer was dried overnight over anhydrous $MgSO_4$. The solvent was removed with a rotary evaporator to give the crude product. It was purified by recrystallization from methanol. Yield: 80%. Anal. calcd. (%) for $C_{21}H_{23}N_3$: C, 79.21; H, 7.60; N, 13.20. Found (%): C, 79.19; H, 7.63; N, 13.17. ESI-MS: $m/z = 318.3$ (HM^+). IR (KBr, cm^{-1}): 3416 (m), 1601 (s), 1521 (s), 1480 (w). Single crystals of L were obtained by slow evaporation of a benzene solution at room temperature.

2.4. Synthesis of $Zn(SCN)_2L_2$

The tetrahedral zinc complex was readily prepared by layering method at room temperature. A clear methanol solution (15 mL) of $Zn(NO_3)_2 \cdot 6H_2O$ (29.80 mg, 0.1 mmol) and NaSCN (16.40 mg, 0.2 mmol) was carefully layered onto a solution of L (73.40 mg, 0.2 mmol) in chloroform (15 mL). Yellow needle-shaped crystals suitable for X-ray diffraction were obtained by slow interlayer diffusion. Yield: 70%. Anal. calcd. (%) for $ZnC_{44}H_{46}N_8S_2$: C, 64.73; H, 5.68; N, 13.77. Found (%): C, 64.78; H, 5.64; N, 13.81. IR (KBr, cm^{-1}): 3421 (m), 2073 (s), 1595 (s), 1524 (s), 1425 (w).

2.5. X-ray crystal structure determination

The X-ray diffraction measurements were performed on a Bruker SMART CCD area detector using graphite monochromated MoKα radiation ($\lambda = 0.71073$ Å) at 298(2) K. Intensity data were collected in the variable ω-scan mode. The structures were solved by direct methods and difference Fourier syntheses. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were introduced geometrically. Calculations were performed with SHELXTL-97 program package [16]. Details of the crystal parameters, data collections and refinements are listed in Table 1, and selected bond distances and angles are given in Table 2.

Table 1
Crystallographic for L and $Zn(SCN)_2L_2$

Compound	L	$Zn(SCN)_2L_2$
Empirical formula	$C_{21}H_{23}N_3$	$C_{44}H_{46}ZnN_8S_2$
Formula weight	317.42	816.38
Temperature (K)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1$
a (Å)	8.777(9)	19.413(3)
b (Å)	7.701(8)	10.471(1)
c (Å)	13.64(1)	21.760(3)
β (°)	106.31(2)	108.411(3)
Volume ($Å^3$)	885.0(2)	4197(1)
Z	2	4
ρ_{Calcd} (g/cm^3)	1.191	1.292
$F(000)$	340	1712
Crystal size (mm)	0.35 × 0.29 × 0.14	0.22 × 0.13 × 0.06
Reflections collected	4342	21643
Unique reflections	2659	7408
Parameters	230	496
S on F^2	1.001	1.015
R_1 [$I > 2\sigma(I)$]	0.0710	0.0508
wR_2 [$I > 2\sigma(I)$]	0.1387	0.1112
R_1	0.2165	0.1158
wR_2	0.1846	0.1423
$\Delta\rho_{min/max}$ [e. nm^{-3}]	0.0163/−0.0187	0.0517/−0.0298