



Research Article

Synthesis, characterization and single crystal X-ray analysis of azobenzene-4, 4'-dicarbonyl chloride

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Abstract

The title compound azobenzene-4, 4'-dicarbonyl chloride has been synthesized in distilled dichloromethane and characterized by elemental analysis (C, H, N), IR and NMR (¹H & ¹³C) studies. The crystal and molecular structure was further confirmed using single crystal X-ray diffraction analysis. It was crystallized in triclinic crystal system with space group P-1. The centrosymmetrically related molecules held together via C-H...O secondary interaction result in molecular aggregation of the compound.

Key words: Azo-compounds; photochromic; supramolecular; centrosymmetrically; dihedral angle

Introduction

The synthesis of new and novel materials has long been recognized as essential step in the development of advance technology. It is becoming increasingly urgent to produce materials designed to perform highly specific and cooperative functions. In this context, the design and synthesis of azo (-N=N-) group containing compounds has led remarkable developments in that direction owing to their potential applications in the construction of metal-organic frameworks (Chen *et al.*, 2008), as chemosensors (Lee *et al.*, 2007) and photoactive materials (Park *et al.*, 2012). The azo functionalised MOFs are exploited as materials for selective capture of CO₂ (Nagaraja *et al.*, 2012). The azo-loaded chemosensors are used to detect cations (Arabahmadi & Amani, 2013), anions (Lee *et al.*, 2001) and neutral molecules (Goshwami *et al.*, 1999) while the azo-

based photoactive materials are used for photoresponsive molecular recognition (Hunter *et al.*, 2004), light driven fluorescence enhancement (Man & Hara, 2005), design of molecular photoswitches (Willner & Rubin, 1996) and photoinduced release of adsorbed CO₂ (Park *et al.*, 2012). The azo-based systems have also been exploited as photoactive DNA cleavage agents (Panja *et al.*, 2011).

In 1937, G. S. Hartley published a study of the influence of light on the configuration of N=N double bonds (Hartley, 1937). The exposure of light to a solution of azobenzene in acetone to light allowed the discovery of the *cis* isomer. This finding was the starting point of the development of one of the best organic molecular switches described so far.

In recent years, the photochromic properties of azobenzenes have attracted great interest owing to the isomerization of N=N bonds that occurs readily in the presence of a light

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source (Ross & Blanc, 1971). The introduction of an azobenzene fragment in a molecule with biological activity, can allow the spatial and temporal control of a variety of biological processes. The isomerization of azo-compounds has been used as a synthetic tool to control the opening and closing of pores in cellular membranes, essential for the transport of ions (Banghart, 2004).

Considering these aspects, the present article is thought to be of worth as it deals with the synthesis and characterization of azobenzene-4, 4'-dicarbonyl chloride. It also includes single crystal X-ray analysis to confirm the molecular structure of the compound.

Experimental Section

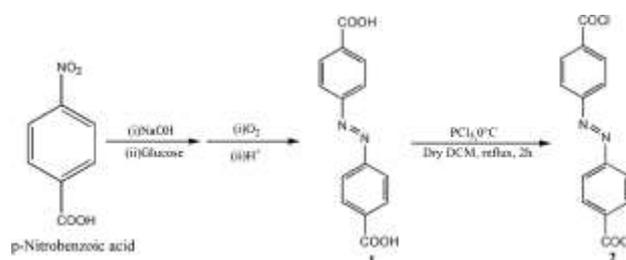
All reagents and solvents were commercially available and used as received. The carbon, nitrogen, and hydrogen contents of the compounds were determined by Carbo-Erba elemental analyzer 1108. The infrared spectra of the compounds were recorded on a Varian 3100 FT-IR spectrometer ($4000\text{--}400\text{cm}^{-1}$) using KBr disks.

^1H and ^{13}C NMR spectra of compounds were recorded using JEOL AL 300 MHz spectrometer. The starting compound azobenzene-4, 4'-dicarboxylic acid **1** and azobenzene-4, 4'-dicarbonyl chloride **2** were synthesized following reported methods used (Ghosh *et al.*, 2008).

Synthesis of azobenzene-4, 4'-dicarboxylic acid 1: For the synthesis of H₂ADA, *p*-Nitrobenzoic acid (15 g, 67.5 mmol) and NaOH (50 g, 1.25 mmol) were mixed in water (225 mL), and the solution was heated on a water bath until the solid dissolved; hot aqueous glucose (100 g in 150 mL of water) was then added slowly into the above mixture at 50 °C whereupon a yellow precipitate was obtained, which immediately changed to a brown solution upon further addition of glucose. This reaction was highly exothermic. Then, a stream of air was passed into the mixture for 3 h and a light brown precipitate was obtained. This was filtered, dissolved in water, and acidified with acetic acid (25 mL) whereupon a light pink precipitate was obtained. This was filtered, washed with plenty of water (300 mL), and dried in a desiccator to obtain H₂ADA as a brownish orange powder. The analytical data of the compound **1** are as follows: Brownish orange solid, yield 80%, m.p. 335 °C, IR (KBr) νcm^{-1} : 1683(C=O), 1600(N=N); ^1H NMR(CDCl₃) δ : 13.3 (2H, s, COOH), 8.16 (4H, *J*= 8.4 Hz, d, Ar), 8.01 (4H, *J*= 8.1 Hz, d, Ar); ^{13}C NMR (CDCl₃) δ : 166(COOH), 154(Ar), 133(Ar), 130(Ar), 122(Ar); analysis for C₁₄H₁₀N₂O₄: 58.53 (58.34), 4.06 (4.53), 11.38 (11.04).

Synthesis of azobenzene-4, 4'-dicarbonyl chloride 2: For the synthesis of ACCL, to a suspension of azobenzene-4, 4'-dicarboxylic acid (1 g, 3.7 mmol) in 20 mL of 1, 2-dichloromethane was added 2.0 g PCl₅ at 0 °C and then refluxed for 2h. The red precipitate obtained was filtered and dried. It was recrystallized by mixture of

DMF/methanol. Single crystal suitable for X-ray was obtained by layering the solution of compound in DMF with methanol. The analytical data of the compound **2** are as follows: Red solid, yield 75%, m.p. 158 °C, IR (KBr) νcm^{-1} : 1776(C=O), 1601(N=N); ^1H NMR(CDCl₃) δ : 8.30 (d, *J*=8.7 Hz, 4H, Ar), 8.05 (d, *J*=8.7 Hz, 4H, Ar); ^{13}C NMR (CDCl₃) δ : 167 (C=O), 155 (C-N=N), 135 (C-C=O), 132 (Ar), 123 (Ar); analysis for C₁₄H₈N₂O₂Cl₂: 54.75 (54.33), 2.63 (2.54), 9.12 (9.14).



Scheme 1. Synthetic strategy of **1** & **2**

Single crystal X-ray analysis of 2: For X-ray Crystallographic Study, the X-ray diffraction data were collected by mounting a single crystal of the sample on glass fibers. Oxford diffraction XCALIBUR-EOS diffractometer was used for the determination of cell parameters and intensity data collection at room temperature. Monochromating Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) was used for the measurements. The crystal structures were solved by direct methods using SHELXS-97 Program (Sheldrick, 1997) and were refined by full matrix least-squares SHELXL-97 (Sheldrick, 1990). Drawings were carried out using MERCURY (Bruno *et al.*, 2002) and special computations were carried out with PLATON (Spek, 2003).

Results and Discussion

The infrared spectra of **1** and **2** show peaks at 1683 and 1776 cm^{-1} due to C=O stretching vibrations respectively. The peaks at 1600 and 1601 cm^{-1} correspond to N=N stretching vibrations of **1** and **2**. ^1H NMR spectra exhibit peaks at $\delta = 13.3$ due to COOH proton of **1**. ^{13}C NMR spectra of **1** and **2** exhibit peaks at $\delta = 166$ and 167 ppm due to C=O carbon respectively.

Crystallographic data and refinement details for the structural analyses of **2** are summarized in Table 1. Selected bond lengths and bond angles with their estimated standard deviations are presented in Table 2, while selected parameters for weak interactions are listed in Table 3. Crystallographic data for the title compound **2** reported in this paper have been deposited with the Cambridge data centre. The deposition number is CCDC 1846836. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/.

Table 1: Crystal data and refinement detail for **2**

Parameters	2
formula	C ₁₄ H ₈ Cl ₂ N ₂ O ₂
M	307.12
Crystal system	triclinic
Temperature/K	293
Space group	P-1
a(Å)	3.8460(4)
b(Å)	17.1186(18)
c(Å)	20.5463(18)
α(deg)	92.689(8)
β(deg)	92.788(8)
γ(deg)	95.713(8)
V(Å ³)	3442.6(2)
Z	4
D _c (mg m ⁻³)	1.359
Absorption coefficient	0.283 mm ⁻¹
F(000)	568
Reflns collected/unique	11265/5987
R(int)	0.0400
Index ranges	-3<=h<=5, -18<=k<=21 -26<=l<=24
Refinement method	full-matrix, least-squares on F ²
FinalR indices [I>2σ(I)] ^a	R1=0.0585,wR2=0.0845
R indices (all data)	R1=0.1691,wR2=0.1207
GOF on F ² (GOF) ^a	0.960

Table 2: Selected bond length (Å) and bond angles (deg) for **2**

Cl(05)-C(20)	1.780(4)	C(10)-C(20)-O(03)	125.6(4)
N(03)-N(03)	1.225(4)	C(10)-C(20)-Cl(05)	118.4(3)
N(03)-C(41)	1.440(4)	O(03)-C(20)-Cl(05)	117.4(3)
C(20)-O(03)	1.178(4)	C(12)-C(41)-C(03)	115.4(3)
C(10)-C(20)	1.480(4)	C(01)-C(41)-N(03)	124.1(3)
C(01)-C(05)	1.373(4)	N(03)-N(03)-C(41)	113.4(4)

Fig. 1 shows the ORTEP diagram with atom numbering scheme of **2** while Fig. 2 shows C–H...O secondary interactions.

The X-ray single-crystal structure determination of compound **2** suggested that it was crystallized in triclinic crystal system with space group P-1. The distances

Cl(05)–C(20) (1.780(4) Å) and C(20)–O(03) (1.178(4) Å) fall in the reported range. The dihedral angles between two phenyl rings is 15.3°. It is interesting to note that, centrosymmetrically related molecules connected via C–H...O secondary interaction of 2.651 Å (Table 3) lead to supramolecular associations of molecules in the crystal structure (Fig. 2).

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