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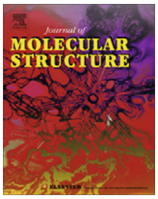

Experimental and theoretical studies of 3-benzyloxy-2-nitropyridine

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HIGHLIGHTS

- ▶ Synthesis of 3-benzyloxy-2-nitropyridine.
- ▶ The compound was characterized by IR, Raman and X-ray crystallography.
- ▶ DFT studies on the structures of the compound.
- ▶ DFT studies on the vibrational frequencies.

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ABSTRACT

The structure of 3-benzyloxy-2-nitropyridine has been investigated both experimentally and theoretically. The X-ray crystallography results show that the nitro group is tilted out of the pyridine ring plane by 66.4(4)°, which is mainly attributed to the electron–electron repulsions of the lone pairs in O atom of the 3-benzyloxy moiety with O atom in nitro group. An interesting centrosymmetric π-stacking molecular pair has been found in the crystalline state, which results in the approximate coplanarity of the pyridine ring with the benzene ring. The calculated results show that the dihedral angle between the nitro group and pyridine ring from the X3LYP method is much closer to the experimental data than that from the M06-2X one. The existing two conformational isomers of 3-benzyloxy-2-nitropyridine with equal energy explain well the disorder of the nitro group at room temperature. In addition, the vibrational frequencies are also calculated by the X3LYP and M06-2X methods and compared with the experimental results. The prediction from the X3LYP method coincides with the locations of the experimental frequencies well.

1. Introduction

In the aromatic nitro compounds without *o*-substituent group, the nitro groups are usually coplanar with the aromatic ring planes, in which the dihedral angles between the nitro groups and the aromatic ring planes are less than 5° [1–3]. In these cases, the molecules are stabilized by the *p*–π conjugation. However, the dihedral angles between the nitro group and the aromatic ring planes are varied from 10° to 70° in some *o*-substituted aromatic nitro compounds [4–6], and even to about 90° in some *o*,*o*′-disubstituted ones such as 84(1)° in 1,3,5-triisopropyl-2-nitrobenzene [7]. The large dihedral angle is generally attributed to the steric effect of the *o*-substituent [8]. For example, in 2-[(4-methylphenylimino)methyl]-1-nitrobenzene, the nitro plane is tilted out of the benzene ring plane by 27.9(5)° to minimize the steric hindrance between the ortho atoms of the nitro group and their vicinal H atoms [9].

The molecular structures of 3- and 4-nitropyridine derivatives have been extensively reported [10,11]. However, the molecular structures of 2-nitropyridine derivatives are seldom investigated. The title compound, 3-benzyloxy-2-nitropyridine (**BNP**, Scheme 1), is an important intermediate for the synthesis of asymmetric cyanine dyes for the fluorescence detection of nucleic acids [12]. In this paper, the molecular structure of **BNP** was determined by X-ray single crystallography. The nitro group is disordered, and a very large dihedral angle (66.4°) between the nitro group and the pyridine ring plane was observed. In order to explain these observations, the molecular structure and the rotational barrier of the nitro group were studied theoretically. Moreover, the vibrational spectra of **BNP** were calculated by the X3LYP [13,14] and M06-2X [15] methods.

2. Experimental and theoretical methods

2.1. Materials and general methods

All reagents are commercially available and purified by standard methods prior to use. The melting points were measured on

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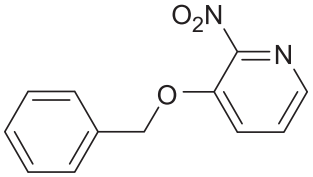

Scheme 1.

Table 1
Crystal data and structure refinement summary for BNP.

Empirical formula	$C_{12}H_{10}N_2O_3$
Formula weight	230.22
Crystal system tetragonal	Monoclinic
Space group	$P2_1/n$
a (Å)	7.112(3)
b (Å)	13.030(6)
c (Å)	12.407(5)
β (°)	92.004(7)
V (Å^3)	1149.0(9)
D_c (g/cm^3)	1.331
F(000)	480
Z	4
μ(Mo Kα)/mm	0.098
θ Range (°)	2.27–25.00
Range of h, k, l	−7/8, −15/13, −14/13
Reflections collected/unique	5774/2029
Data/restraints/parameters	2029/36/172
R and ωR	0.0510 and 0.1522
Goodness-of-fit on F^2	1.022
Max. res. peak and hole (e Å^{-3})	0.131 and −0.185

Table 2
Selected bond lengths (Å) and bond angles (°) for BNP from the experiment and theoretical calculations.

Parameters	M06-2X	X3LYP	Experiment
O(2)—N(2)	1.212	1.221	1.205
O(3)—N(2)	1.204	1.214	1.220
N(2)—C(12)	1.489	1.493	1.494
N(1)—C(12)	1.304	1.309	1.315
O(1)—C(8)	1.337	1.343	1.357
O(1)-C(7)	1.421	1.432	1.431
C(6)—C(7)	1.506	1.507	1.512
O(2)—N(2)—C(12)	116.5	116.5	118.2
O(3)—N(2)—C(12)	117.1	117.2	116.3
O(2)—N(2)—O(3)	126.4	126.3	125.5
C(11)—N(1)—C(12)	117.7	118.0	115.1
C(8)—O(1)—C(7)	118.7	119.4	119.5
O(1)—C(7)—C(6)	108.3	108.8	107.8
O(2)—N(2)—C(12)—N(1)	−130.1	−125.7	−114.8
O(3)—N(2)—C(12)—N(1)	48.6	53.0	66.2
O(2)—N(2)—C(12)—C(8)	49.4	54.0	65.6
O(3)—N(2)—C(12)—C(8)	−131.9	−127.4	−113.3
N(2)—C(12)—C(8)—O(1)	3.8	3.5	1.2
C(1)—C(6)—C(7)—O(1)	−25.6	−29.8	0.8

a Yanagimoto MP-500 apparatus (uncorrected). The FT-IR spectra (KBr pellets and in CCl_4 solvent) were measured on a BIO-RAD FTS 3000 infrared spectrometer in the 4000–400 cm^{-1} range with a 4 cm^{-1} resolution. The FT-Raman spectra were measured using Bruker RFS 100/S FT-Raman spectrometer with a 4 cm^{-1} resolution. The ^{1}H NMR spectra were recorded on a Bruker AV-400 spectrometer (400 MHz) at 298 K in $CDCl_3$. The MS was performed on the Thermo Finnigan Trace DSQ GC–MS spectrometer.

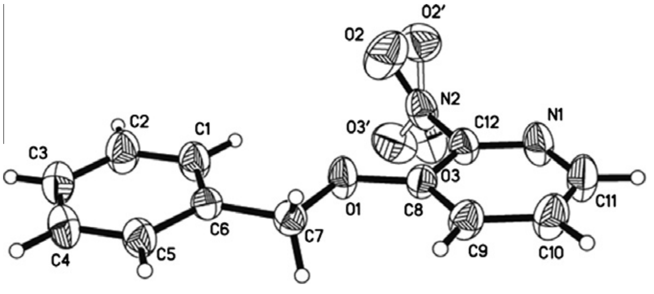

Fig. 1. The crystal structure of **BNP** with atom labels and 30% probability ellipsoids level.

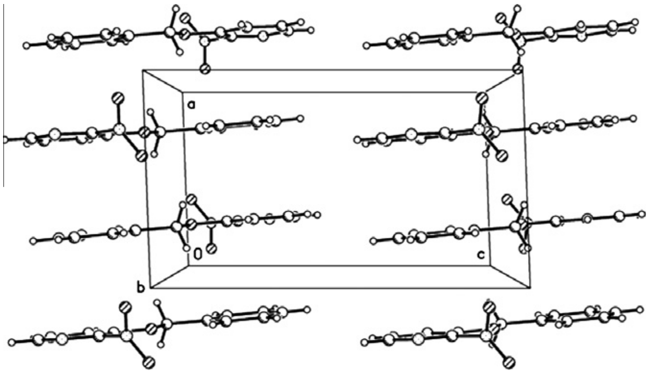

Fig. 2. The crystal packing, viewed along the b axis.

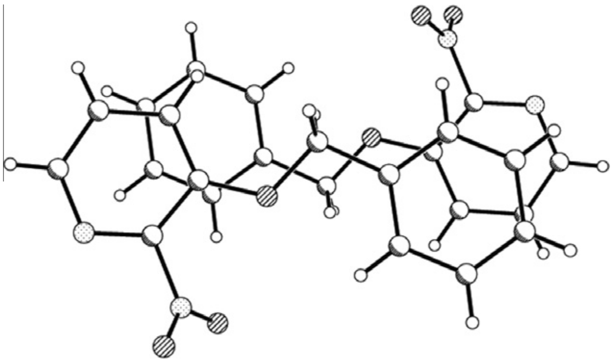

Fig. 3. The centrosymmetric π-stacking molecular pairs.

2.2. Preparation of BNP

2-Nitro-3-hydroxypyridine (2.80 g, 20 mmol) was added to a solution of NaOH (0.80 g, 20 mmol) in 20 ml EtOH and stirred for 1 h at room temperature. The formed sodium salt was collected and air-dried.

A solution of benzyl bromide (2.15 ml, 18 mmol) in 18 ml DMF was added dropwise to the mixture of the above sodium salt (2.93 g, 18 mmol) in 18 ml DMF, and was stirred for 10 h at room temperature. Then the reaction mixture was added 100 ml water, extracted with ethyl ether (3 × 100 ml). The ether phase was dried with anhydrous $MgSO_4$, filtrated, and concentrated to afford crude yellow liquid, which was further purified by chromatography using light petroleum/ethyl acetate (2:1) as the eluant to provide colorless needle crystals (3.03 g, 74.0%), mp. 60–62 °C. ^{1}H NMR ($CDCl_3$): δ 8.06 (d, J = 4.4 Hz, 1H), 7.50 (d, J = 8.4 Hz, 1H), 7.45 (dd, J_1 = 4.4 Hz, J_2 = 8.4 Hz, 1H), 7.41–7.31 (m, 5H). MS: m/z 91 (100, M^+-$NO_2PyO\cdot$), 124 (12.6).

2.3. X-ray crystallography

Single-crystal X-ray diffraction measurements were carried out on a Bruker Smart 1000 CCD diffractometer using graphite