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SYNTHESIS, SPECTROSCOPIC PROPERTIES, AND CRYSTAL STRUCTURE OF 1-NAPHTHYL(1-METHYLETHYLIDENE)IMINIUM CHLORIDE

***Harbi Tomah Al-Masri*, PhD**
***Ziad Moussa*, PhD**
Department of Chemistry, Faculty of Science, Taibah University,
Madinah, Saudi Arabia

Abstract

Condensation of 1-naphthylamine with acetone in the presence of $Et_3N \cdot HCl$ as a catalyst gave the corresponding 1-naphthyl (1-methylethylidene) iminium chloride (**1**). The salt was identified and characterized by multinuclear NMR (^1H and ^{13}C NMR) and IR spectroscopy. In solution, the two methylenic hydrogens of the *N*-isopropyl moiety are anisochronous. This result was confirmed by the X-ray investigation of **1** in the solid state. **1** crystallized in the orthorhombic space group *P*bca, a = 10.8668(8)Å, b = 11.1758(9) Å, c = 18.8726(18)Å, $\alpha = \gamma = \beta = 90$ °, Z = 8. The structure was solved by direct methods, and retined by full-matrix least squares techniques to an *R* factor of 0.0308 for 1874 observed reflections. In the crystal the 1-naphthyl (1-methylethylidene) iminium cation and chloride anion are linked by N–H···Cl hydrogen bond.

Keywords: Iminium salt; Acetone; Crystal structure; Anisochronous; 1-Naphthylamine

1. Introduction

Iminium salts are very useful versatile intermediates and have been well in the area of organic synthesis (Böhme, 1967; Jarrahpour, 2010) and catalytic chemistry (Page, 2007). In addition, some of them have shown a broad spectrum of biological and pharmaceutically activities (Attygalle, 1984; Elliott, 1995; Pichon, 1996). As a continuation of our work on the synthesis and solid-state structures of phosphorus(III) ligands containing naphthyl organic skeletons and direct P–N bonds **(**Al-Masri, 2012; Al-Masri, 2013) ,thereof, we herein report the synthesis, spectroscopic properties, and crystal structure of (**1**).

2. Materials and Methods:

2.1 Chemistry

Infra-red spectra were recorded on a *Shimadzu FTIR-8400S* spectrometer between 4000-400 cm^{-1} using KBr disks. The NMR spectra were recorded at 25 °C on a *Bruker-Avance-DRX-400* MHz NMR spectrometer operating at 400.17 (^1H) and 100.63 (^{13}C) using tetramethylsilane as external standard. Melting point was carried out on a *Gallenkamp* apparatus with open capillaries.

2.2 Preparation of 1-naphthyl(1-methylethylidene)iminium chloride (1)

1-naphthylamine (0.50 g, 3.5 mmol) was added to a stirred solution of acetone (161 ml, 3.5 mmol) in the presence of $Et_3N{\cdot}HCl$ (0.48 g, 3.5 mmol). The mixture was heated to reflux for about 8 h. The precipitate was filtered off and washed with water and ethanol, giving a fine white powder, recrystallization from CH_2Cl_2/hexane (1/2 (v/v)) at 25 °C produced colorless crystals in 70% yield. Mp 130−132 °C; IR (KBr): 1670, 1575, 1240 cm^{-1}; ^1H NMR ($CDCl_3$, δ/ppm): 1.80 (s, 3H), 2.40 (s, 3H), 6.72 (d, J = 7 Hz, lH), 7.38-7.48 (m, 3H), 7.57 (d, J = 8 Hz, lH), 7.75 (d, J = 8 Hz, 1H); ^{13}C NMR ($CDCl_3$, δ/ppm): 21.1, 28.7, 109.9, 114.1, 123.6, 123.9, 125.1, 125.9, 126.6, 128.5,135.5, 148.4, 169.6.

2.3 Data collection and structure determination

Crystallographic data are given in Table 1. Data [$\lambda(Cu_{K\alpha}) = 1.54178$ Å] were collected with a *Bruker-AXS SMART-APEX CCD* diffractometer. All observed reflections were used for determination of the unit cell parameters. Indexing was performed using *SMART* (SMART 5.625, 2001). Frames were integrated with *SAINT* software package (SAINT 6.28A, 2001). Absorption correction was performed by multi-scan method implemented in *SADABS* (Sheldrick, 1997). Crystal structures were solved using *SHELXS-97* and refined using *SHELXL-97* contained in *SHELXTL* and *WinGX-1.70.01* programs packages (Sheldrick, 2008). All non-hydrogen atoms were refined with anisotropic displacement parameters. All H-atoms bonded to carbon atoms were placed in geometrically optimized positions and refined with an isotropic displacement parameter relative to the attached atoms. Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC-**966241** for **1** (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

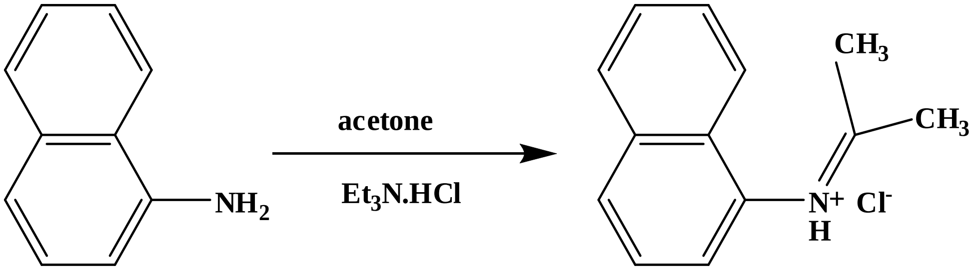
Table 1: Crystal data and structure refinement for **1**

Formula	$C_{13}H_{14}N^{+}.Cl^{-}$	Z	8
M_r	219.70	ρ_{calcd} [Mg m^{-3}]	1.273
Temp (K)	296(2)	F(000)	928
Crystal system	orthorhombic	Abs coeff [mm^{-1}]	2.650
Space group	P*b*ca	No. of rflns coll.	16489
a [Å]	10.8668(8)	No.of indep rflns	1874
b [Å]	11.1758(9)	R_{int}	0.0300
c [Å]	18.8726(18)	No. of params	142
α [°]	90.00	$R1$ (I>2σ (I))	0.0308
β [°]	90.00	w$R2$ (all data)	0.0803
γ [°]	90.00	$(\Delta/\rho)_{max}$ [e.Å^{-3}]	0.428
V [Å^3]	2292 (3)	$(\Delta/\rho)_{min}$ [e.Å^{-3}]	-0.185

3. Results and Discussion:

3.1 Synthesis

Scheme 1 summarizes the synthesis of **1**. The direct reaction of 1-naphthylamine with acetone in the presence of $Et_3N.HCl$ afforded **1** in 70% yield.



Scheme 1: Preparation of **1**

3.2 ^{1}H and ^{13}C NMR Spectra

The ^{1}H and ^{13}C NMR spectra of the two methyls of the *i*-propyl group in **1** showed two signals at δ = 1.80 and 2.40 ppm and at δ = 21.1 and 28.7 ppm, respectively. Indicating that the two methyls of the N-isopropyl group are anisochronous, presumably due to a frozen $N{=}CMe_2$ rotation. The nonequivalence of these methyls is confirmed by the X-ray structure determination of **1**.

3.3 Molecular Structure of 1

Colorless crystals of **1** were obtained as described in *Experimental Section*. Compound **1** crystallizes in the orthorhombic space group *P*bca. Selected interatomic distances and angles are collected in *Table 2*. The molecular structure is depicted in *Figure 1*.

Table 2: Selected bond lengths (Å) and bond angles (deg.) for **1**

C(1)–N(1)	1.488(2)	C(11) –C(12)	1.477(2)
C(11)–N(1)	1.288(2)	C(1)–N(1)–C(11)	126.0(1)
C(11)–C(12)	1.481(2)	C(9)-C(1)-N(1)–H(1)	-88.0(2)
C(11)–C(13)	1.477(2)	C(8)-C(9)-C(1)–N(1)	-6.1(2)
H(1)–N(1)	0.98(2)	C(9)-C(1)-N(1)–C(11)	90.7(2)
C(11) –C(12)	1.481(2)	∑ angles at N(1)	360.0

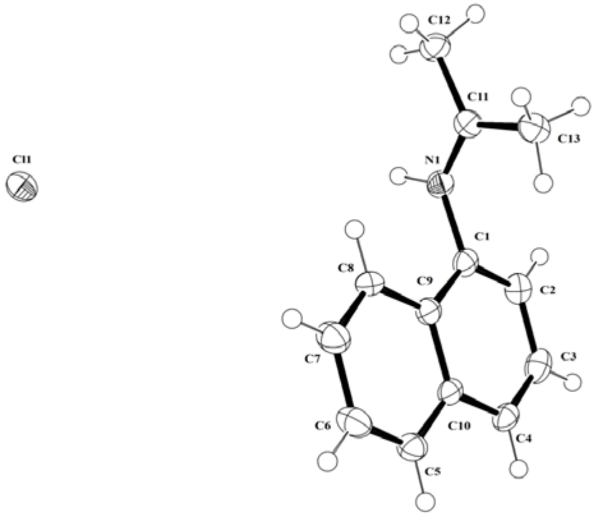


Figure 1: An *ORTEP* view of **1**, showing 50% probability displacement ellipsoids and arbitrary spheres for the hydrogen atoms.

Table 3: Hydrogen-bond geometry (Å,°)

D−H···*A*	*D*−H	H···*A*	*D*···*A*	*D*−H···*A*
N1−H1···Cl1	0.99(2)	2.05(2)	3.0273(14)	170.7(19)

Symmetry code: -x +1/2, y +1/2, z

The C-napthyl skeleton in **1** is almost planar, and the nitrogen atom resides almost in the C-napthyl plane [torsional angle C(8)−C(9)−C(1)−N(1) - 6.1(2)°]. The directions of the C(11)−N(1) and H(1)−N(1) bonds are virtually perpendicular to the C-napthyl plane [C(9)−C(1)−N(1)−C(11) 90.7(2)° and C(9)−C(1)−N(1)−H(1) - 88.0(2)°, respectively] (*Table 2*). The *N*-isopropyl moiety tilted away from the plane of naphthalene and the two methyls occupy two positions that are not symmetric with respect to the plane of naphthalene, in agreement with spectroscopic data.

The C(11)–N(1) [1.288(2) Å] bond length is significantly shorter than the C(1)–N(1) [1.488(2) Å] bond length which agrees with the C(11)=N(1) double bond. The C(11)=N(1) and C(1)–N(1) bond distances in **1** are within the expected value range and significantly longer than those reported for 2,2-[1,4-phenylenebis(methylenethio)]-dithiazole [1.299(3); 1.385(3) Å] (Wei,

2003) and 4-{[5-methyl-2-furyl)methylene]-hydrazinocarbonyl}pyridinium chloride monohydrate [1.2823(17); 1.3314(19) Å] (Li-Min, 2009), respectively. In the crystal structure the iminium and chloride ions are connected by N-H···Cl hydrogen bond. The N···Cl distance [3.0273(14) Å] (*Table 3*) indicating strong interaction between the iminium and chloride ions (Wei, 2003).

The X-Ray crystal structure of **1** (*Figure 1*) shows a trigonal-planar three-coordinate nitrogen (angle sum at nitrogen 360.0°) atom. The aromatic ring in **1** as expected has usual bond lengths and angles.

4. Conclusion

In conclusion, we have shown the successful synthesis of 1-naphthyl(1-methylethylidene)iminium chloride (**1**). The new compound was characterized by IR and multinuclear NMR spectroscopy. The two methyls of the *N*-isopropyl group are anisochronous, as indicated by ^{1}H and ^{13}C NMR spectroscopy and confirmed by crystal structure determination for **1**.

References:

H. Böhme, H. G. Viehe, *Iminium Salt in Organic Chemistry*, Wiley, New York, **(**1976).
A. Jarrahpour, M. Zarei, *Tetrahedron* 66, 5017 (2010).
P. C. B. Page, M. M. Farah, B. R. Buckley, A. J. Blacker, *J. Org. Chem.* 72 (2007) 4424.
A. B. Attygalle, E. D. Morgan, *Chem. Soc. Rev.* 13 (1984)245.
R. L. Elliott, H. Kopecka, N. -H. Lin, Y. He, D. S. Garvey, *Synthesis* 772 (1995).
M. Pichon, B. Figadere, *Tetrahedron: Asymmetry* 7 (1996) 927.
H. T. Al-Masri, A. H. Emwas, Z. A. Al-Talla, M. H. Alkordi, *Phosphorus Phosphorus, Sulfur, Silicon Relat. Elem.* 187 (2012) 1082.
H. T. Al-Masri, *Synth. React. Inorg., Met.-Org. Chem.* 43 (2013) 102.
H. T. Al-Masri, *Z. Anorg. Allg. Chem.* 638 (2012) 1012.
H. T. Al-Masri, B. M. Mohamed, Z. Moussa, M. H. Alkordi, *Helv. Chim. Acta* 96 (2013) 738.
SMART 5.625, Indexing Program, Bruker AXS Inc., Madison, WI, (2001).
SAINT 6.28A, Data Reduction Program, Bruker AXS Inc., Madison, WI, (2001).
G. M. Sheldrick, *SADABS-a Program for Empirical Absorption Correction*, University of Göttingen, Germany, (1997)..
G. M. Sheldrick, *SHELXTL 6.10, Programs for Crystal Structure Analysis*, Bruker AXS Inc., Madison, WI, (2008).
Z. Wei, L. Hui-Min, L. Chun-Bao, Z. Wen-Qin, *Acta Cryst*. E65 (2003)26.
L. Li-Min, J. Fang-Fang, L. Li, *Acta Cryst*. E65 (2009) 1983.