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NMR, X-RAY AND IR STUDIES OF (E)-3-(PHENYLIMINO)PETAN-2-ONE {ArN(CH_2(C-Me)$_2$O} (Ar = C_6H_5)

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ABSTRACT

A range of new Schiff bias compounds such (E)-3-(phenylimino)petan-2-one {ArN(CH2(C-Me)2O} (Ar = C6H5) contion the chelating imino and oxygen in position α- has been prepared, and structurally characterized in several cases.Well-defined (E)-3-(phenylimino)petan-2-one {ArN(CH2(C-Me)2O} (Ar = C6H5) was obtained by stoichiometric addition of {ArNH2} (Ar = C6H5) and {CO(CH(CH3))2CH2CO} in n-propanol at reflex temperature. IR, NMR and X-ray studies have been obtained for this compound.

Keywords: Schiff bias compounds, (E)-3-(phenylimino)petan-2-one, chelating imino and oxygen, IR, NMR and X-ray studies.

INTRODUCTION

Schiff bias serial have been focus in the last few years ago, especially after reactions with transition metals to forward complexes. Copolymerization of ethylene and amides are widespread in the literature, but this interest is largely confined to the past ten years. Gibson et al. have reported the synthesis, characterisation, and the formation of coordinated mono-alkyl magnesium complexes by reaction of β-diketimine with dimethylmagnesium in 1:1 molar ratio in diethyl ether.1 Also Qing and his group reported the synthesis β-diketiminate ligands, which used as ligand with titanium salt to offered bis(β-diketiminato)titanium complexes [ArNC(CR3)(CHC(CR3)NAr]2TiCl2 (R= F, Ar = 2,6-diisopropylphenyl) and then were examined as catalysis for polymerisation.2 A new 1,4,5,8-naphthalendiimide group and its Pt(II) phosphine complexes are reported by Julia et al.3 A serial of amido-imine bisphenol Schiff-base reacted with manganese salt to offered Manganese amido-imine bisphenol hangman complexes were prepared by Nocera et al.[4]

EXPERIMENTAL

Synthesis of (*E*)-3-(phenylimino)petan-2-one (3)

To a solution of aniline (2 g, 21 mmol) (1) in n-propanol (30 ml) and then (2.15 g, 21 mmol) of n-bromosecinimide (2) in solution was added wise in room temperature. The reaction mixture was stirred with reflex overnight. The mixture was concentrated in vacuum and then was dried over sodium sulphate anhydrite. Colourless crystals were obtained after crystallisation from Et2O at room temperature (2.0 g, 11.283 mmol, 50%).

Characterising data for **3**: ^{1}H NMR (Chloroform-*d*), δ_H 12.7 (s, 1H, *H*N-Ar), 7.15 (m, 5H, *Ar*), 5.2 (s, 2H, C*H*), 2.2 (s, 3H, CH_3), 1.9 (s, 3H, CH_3).

^{13}C NMR (chloroform-*d*) δ_C 155.3 (C=O), 140(C(NHAr), 130, 125, 123 (C_6H_3NH), 90 (NC(Me)CH_2C(Me)CO), 30, 25 (2Me).

Spectroscopic Techniques:

^{1}H, ^{13}C NMR spectra of **3** was acquired at El-Manar university Tunisia on a Bruker Spectrospin AG 300DPX and operating at 300.13 MHz for ^{1}H measurements, 75.47 MHz for ^{13}C measurements.

Chemical shifts are reported in ppm and referenced to the solvent peaks. Coupling constants are quoted in Hertz (Hz).

Single crystal X-ray structural determinations was carried out at El-Manar university Tunisia by Dr. M. Graia; Structures are drawn in the text throughout as the structure was solved by the direct method using SHELXS97[5] and subsequent difference Fourier syntheses and then refined by full-matrix least-squares method on F^2 using SHELXL97[5] Refinement of $\mathbf{F^2}$ against all reflections. The weighted R-factor wR and goodness of fit S are based on $\mathbf{F^2}$, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2$ sigma(F^2) is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on all data will be even larger.

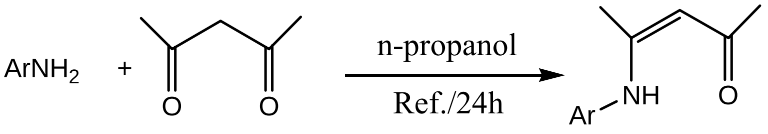
The IR spectrum was recorded on a Parkin-Elmer (4000-400 cm^{-1}) in ATR diamond. Electronic spectra was recorded at room temperature on UV-Vis spectrophotometer mini 1240- Shimadzu.

Reagents and Materials:

High purity aniline, high purity acetylacetone after distilled prior to use. Aniline, acetylacetone and n-propanol were purchased from Hassco Belgium, Riedel-deHaen and Avonchem respectively.

RESULTS AND DISCUSSION

In the present work the effect of changing the steric environment was examined by metathesis of $ArNH_2$ **1** with the acetylacetone **2**, to offering (*E*)-3-(phenylimino)petan-2-one **3**. This was achieved by slowly adding a solution of **1** to **2** in n-propanol at high temperature followed by overnight stirring; work-up yielded $\{ArN(CH_2(C\text{-}Me)_2O\}$ (Ar = C_6H_5) (Ar = 2,6-Pri2C6H3) **3** as colourless crystalline material in 75 % yield after slow cooling of the Et2O solution to -20 ^{o}C, which was confirmed by NMR and X-ray. (Scheme 1).



1 **2** **3**

Ar = C_6H_5

Scheme 1

An X-ray structure determination of **3** confirmed the clearly of the amino is attached to terminal carbon of the acetylacetone and the inclusion of one hydrogen unit (Fig 2). The N-C24 separation has an value of 1.373 (3) Å, a value which is comparable to the three other structurally characterised Ruthenium hydrazide based $(OC(CH_3)NNCH(C_6H_5))$ known.[6] Interestingly, the angle between C24-N-C29 is 124.74 (18)^{o}; the sum of the angles around each carbon (C1, C24 and C29) are close to 360^{o}. The aryl group is perpendicular to the flexible amino propane backbone to protect the open coordination sites in case to worked to metal centre, as shown in Fig. 2); Perspective view of (**3**). Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by spheres of arbitrary radius. The other bond lengths and angles are unremarkable and a selection appears in Table 1. Figure 3 Molecular packing of **3** viewed down the a, *b and c* axes as taken from Diamond demonstration version program.

Compound **3** was examined by IR spectrum. The assignments of the characteristic stretching frequency of *v*(N-H) and *v*(N-C(Me)) at 2240.79 and 2998.66 cm^{-1}, respectively *v*(NC(Ar)) (2120 cm^{-1}), and *v*(C=O) at 1591.73cm^{-1} seems comparable the spectrum to those given for the stretching of (3-methoxybenzoyl)-N-(3-hydroxy phenyl)thiourea.[7]

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In solution **3** behaviour as shown in room temperature ^{1}H NMR spectrum in chloroform-d_1. The peak arising from the ArNH group are resolvable (δ = 12.7 ppm) suggesting that they are joint to the C(Me)CH_2C(Me)O. Also other important peaks are arising as given above. In meantime carbon 13 showed the pick at 140 which is indicate to (C(NHAr).

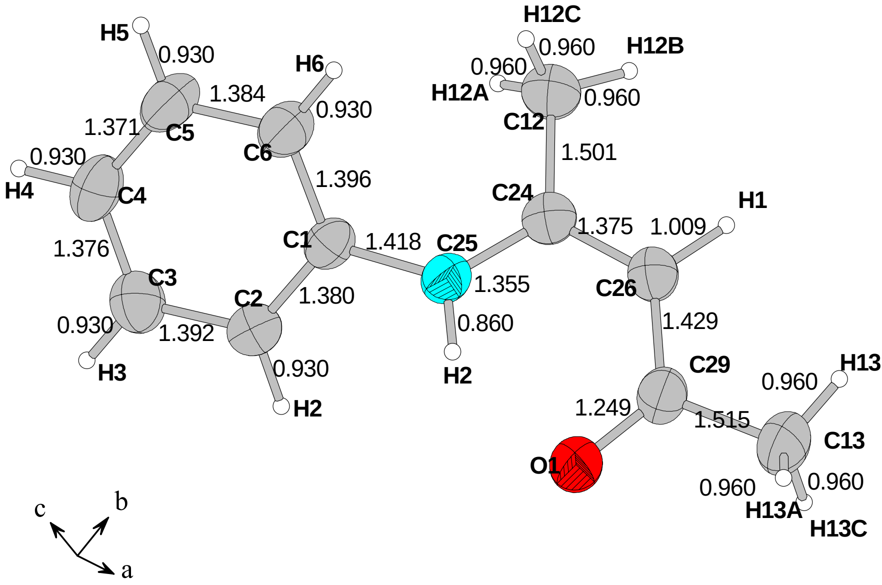

Fig.-2: Molecular structure of 3.

Table-1: Selected bond lengths and angles in **3**

Bond	Length/(Å)	Fragment	Angle/(□)
O1—C29	1.252 (2)	C24—C25—C1	131.21 (16)
C25—C24	1.357 (2)	C25—C24—N26	120.07 (17)
C25—C1	1.417 (2)	C25—C24—C12	120.02 (16)
C24—N26	1.373 (3)	N26—C24—C12	119.86 (18)
C24—C12	1.502 (3)	C24—N26—C29	124.74 (18)
N26—C29	1.430 (3)	O1—C29—N26	123.49 (18)
C29—C13	1.512 (3)	O1—C29—C13	118.66 (18)
C1—C2	1.383 (3)	N26—C29—C13	117.84 (18)

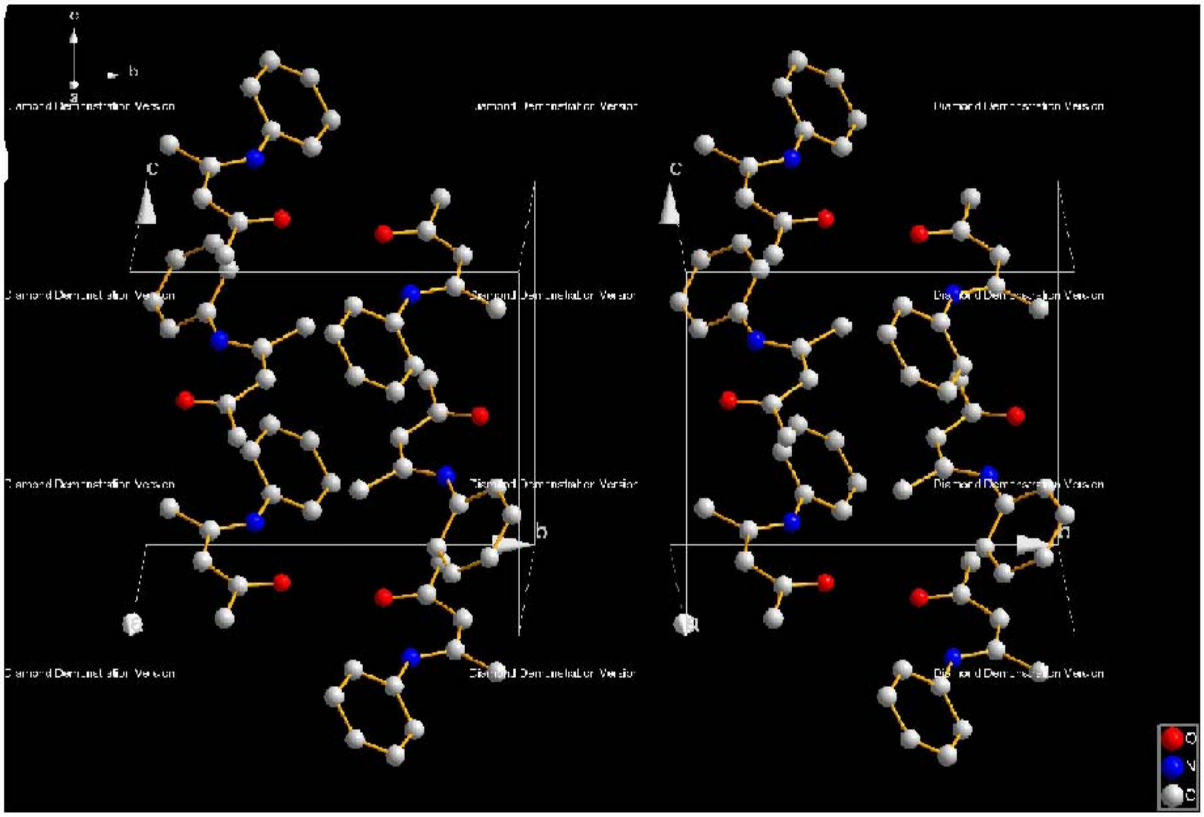

Fig.-3: Molecular packing of **3**.

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