Giuliana Gervasio, Domenica Marabello*

Dipartimento di Chimica I.F.M., Università di Torino,
Via P. Giuria 7, 10125 Torino, Italy

Claudia Barolo, Pierluigi Quagliotto, Guido Viscardi

Dipartimento di Chimica Generale ed Organica Applicata, Università di Torino,
C.so M. D'Azeglio 48, 10125, Torino, Italy.
Received August 8, 2002

The X-ray analyses of some neutral and cationic derivatives of 2-(4-methylpyridin-2-yl)-1H-benzimida-zole are reported and the structural data tentatively correlated to relative UV-visible properties. A rotation of the γ-picoline ring with respect to the benzimidazole moiety may be responsible of the spectral behavior.

Introduction.

Heterocyclic rings, assembled by C-C bonds, of general formula **I**, show applications in many fields [1]; such compounds contain the pyridylideneimino chromogen, evidenced with bold lines (Scheme 1). An extensive work on their synthesis and on their spectral behavior (UV-visible) was reported [2]. The spectral properties of 2-(4-methylpyridin-2-yl)-1H-benzimidazole (X=NH) (**1**) and of some neutral and cationic derivatives were tentatively correlated to a rotation of the γ-picoline ring chromogen group with respect to the benzimidazole moiety; the distortion from planarity was attributed to steric and/or electrostatic repulsion [3].

Scheme 1

X = O, S, Se, NH, NR
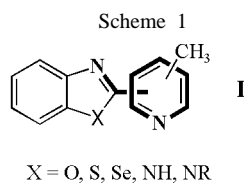
A selected series of 2-(4-methylpyridin-2-yl)-1H-benzimidazole derivatives (**1-5**), has been synthesized recently;
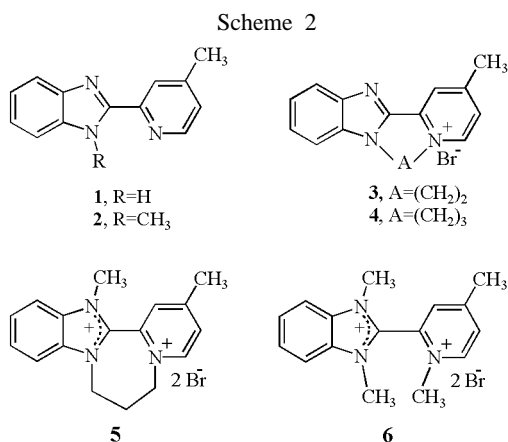
their synthesis, ^{1}H nmr, and ir spectra were reported and discussed in part II of the work [1]. In Scheme 2 compounds **1-5** and the related compound **6** are schematized.

In the present part, X-ray analyses of compounds **2-5** are reported in order to elucidate crystal and molecular structures, useful for interpretation of corresponding uv-visible, and for CNDO/S calculations. Compound **1** gave no suitable crystals for X-ray analysis.
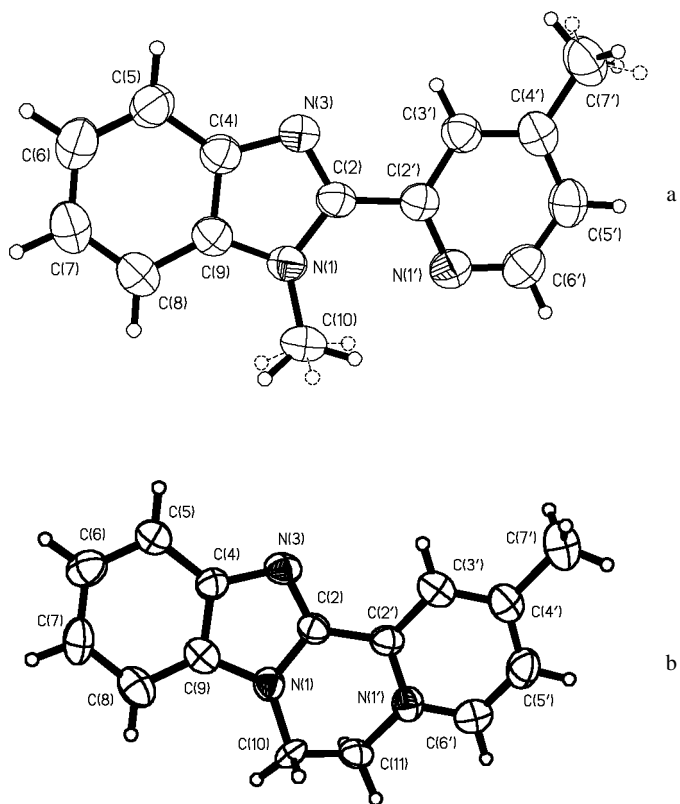
Scheme 2

1, R=H
2, R=CH₃

3, A=(CH₂)₂
4, A=(CH₂)₃

5

6

Figure 1. ORTEP plot (50% probability) of compound **2** $C_{14}H_{13}N_3$ (a) and of salt **3** $[C_{15}H_{14}N_3]^+$ Br⁻(b). Br⁻ ion is omitted for clarity.
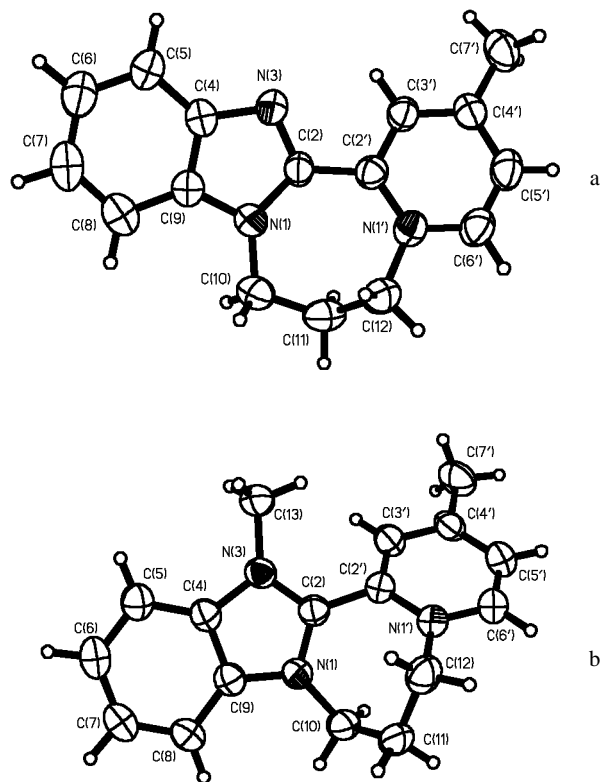
Figure 2. ORTEP plot (50% probability) of salt **4** [$C_{16}H_{16}N_3$]$^+$Br$^-$ (a) and of salt **5** [$C_{17}H_{19}N_3$]$^{2+}$[Br$^-$]$_2$•3H$_2$O (b). Br$^-$ ion and H$_2$O molecules are omitted for clarity.

Table 1

Bond Lengths [Å] and Angles [°] for Compounds **2-5**

Compound	2	3	4	5
N(1)-C(2)	1.377(2)	1.364(10)	1.383(5)	1.331(5)
N(1)-C(9)	1.379(2)	1.390(10)	1.382(6)	1.383(5)
N(1)-C(10)	1.458(2)	1.422(11)	1.465(6)	1.470(5)
N(3)-C(2)	1.319(2)	1.314(10)	1.327(5)	1.340(5)
C(2)-C(2')	1.475(2)	1.444(11)	1.462(6)	1.471(6)
N(3)-C(4)	1.378(2)	1.384(10)	1.384(5)	1.388(5)
N(1')-C(2')	1.339(2)	1.355(10)	1.351(5)	1.367(5)
N(1')-C(6')	1.340(2)	1.316(10)	1.359(5)	1.345(5)
N(1')-C(11)		1.483(10)		
N(1')-C(12)			1.488(6)	1.476(6)
C(2)-N(1)-C(9)	106.17(10)	105.3(6)	105.7(4)	108.7(3)
C(2)-N(1)-C(10)	130.03(12)	123.7(7)	132.4(4)	123.2(3)
C(9)-N(1)-C(10)	123.76(11)	130.4(7)	121.9(4)	127.8(4)
N(3)-C(2)-N(1)	112.78(11)	115.0(7)	112.6(4)	110.2(3)
N(3)-C(2)-C(2')	121.86(11	125.7(7)	117.1(4)	126.8(4)
N(1)-C(2)-C(2')	125.35(11)	119.3(7)	130.3(4)	122.9(4)
C(2)-N(3)-C(4)	105.20(11)	103.4(7)	105.6(4)	107.6(3)
C(2')-N(1')-C(6')	116.11(12)	120.6(7)	121.1(4)	118.9(4)
C(2')-N(1')-C(11)		119.1(7)		
C(6')-N(1')-C(11)		120.1(7)		
C(2')-N(1')-C(12)			122.1(4)	120.8(4)
C(6')-N(1')-C(12)			116.7(4)	120.3(4)

Results and Discussion.

The reaction of base **1** with methyl iodide supplied the N-methyl derivative **2**, while monosalts **3** and **4** were obtained by reaction of base **1** with 1,2-dibromoethane and 1,3-dibromopropane respectively. The reaction of compound **2** with 1,3-dibromopropane gave the bridged bis-quaternary salt **5**. Details on their syntheses are reported in reference 1. Figure 1 shows a view of compounds **2** and **3**, and in Figure 2 compounds **4** and **5** are reported. Relevant bond lengths and angles for compounds **2-5** are listed in Table 1.

For compound **2** ($C_{14}H_{13}N_3$, Figure 1a) two isomers, with the methyl groups in a *syn-* or *anti*-configuration, can exist; in the examined crystal only the *anti*-configuration is present. With the aid of simple force field provided by the MOLDRAW program [4], we analyzed the energy profile of the scans of the N(1)-C(2)-C(2')-N(1') torsion angle. The absolute minimum of energy corresponds to the configuration with the two ring moieties perpendicular with each other, while two maxima correspond to methyl groups in the *syn-* and *anti-* configurations. The two maxima are in a 4/1 ratio of energy, and the small one refers to the found configuration (*anti–*) and the big one to the *syn-*configuration (Figure 3).

The benzimidazole ring, the γ-picoline ring and the methyl group C(10) lie on a plane with the mean deviation from planarity of 0.011 Å, thus allowing a wide electron delocalization in the molecule. A comparison (Table 1) among the N-C bond lengths evidences four types of distance values: 1.319(2) Å [N(3)-C(2)], 1.340(2) Å av. [N(1')-C(2',6')], 1.378(2) Å av. [N(1)-C(2,9) and N(3)-C(4)], and 1.458(2) Å [N(1)-C(10)]. This trend agrees with a decreasing of the double bond character. Also the C-C bond lengths show a variability of values due to different double bond character inside the rings. It is noteworthy the C(2)-C(2') distance (1.475(2) Å) in agreement with a Csp^2-Csp^2 bond [5].
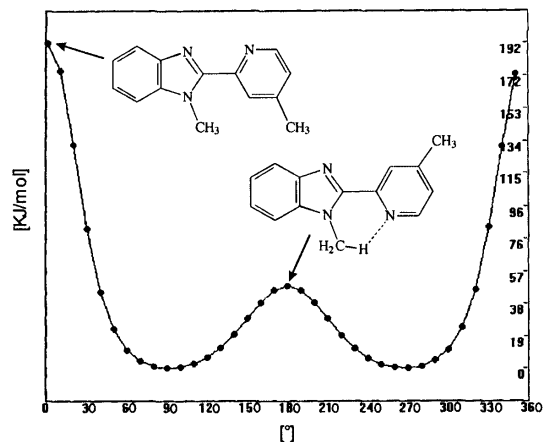

Figure 3. Energy profile (kJ/mol) of the scans of the N(1)-C(2)-C(2')-N(1') torsion angle for compound **2**

Table 2

Intra- and Inter-molecular Hydrogen Bonds in Compound **2**.

Donor···Acceptor [Å]		H···Acceptor[Å]		Donor-H···Acceptor [°]	
C(3')···N(3)[I]	2.839(2)[a]	H(3')···N(3)	2.51	C(3')-H(3')···N(3)	100.2
C(10)···N(1')[I]	2.886(2)[a]	H(10A)···N(1')	2.35	C(10)-H(10A)···N(1')	114.5
C(10)···N(1')[I]	2.886(2)[a]	H(10F)···N(1')	2.25	C(10)-H(10F)···N(1')	122.7
C(5)···N(1')[II]	3.825(2)	H(5)···N(1')	2.96	C(5)-H(5)···N(1')	149.7
C(6)···N(1')[III]	3.551(2)	H(6)···N(1')	2.89	C(6)-H(6)···N(1')	126.6
C(10)···N(3)[IV]	3.527(2)	H(10C)···N(3)	2.67	C(10)-H(10C)···N(3)	148.6
C(10)···N(3)[IV]	3.527(2)	H(10D)···N(3)	2.99	C(10)-H(10D)···N(3)	116.3
C(7')···N(3)[V]	3.511(2)	H(7'C)···N(3)	2.64	C(7')-H(7'C)···N(3)	150.9

Roman numerals refer to the following equivalent positions: I: x,y,z; II: x+1/2, -y+1/2, +z-1/2; III: -x+1/2,+y-1/2,-z+1/2; IV: x+1/2,-y+1/2,+z+1/2; V: x-1,+y,+z. [a] Intramolecular contacts.

An analysis of the crystal packing shows (Table 2) intra- and inter-molecular contacts with distances and angles in agreement with C-H···N hydrogen bonds [6]. The free rotation around the C(2)-C(2') bond and the energy profile (see above) suggests a preference for a perpendicularity of the rings. The intramolecular hydrogen bonds stabilize however the *anti*-planar configuration corresponding to a small maximum of energy (see above) and may justify its presence in the crystalline status.

In compound **3**, of formula $[C_{15}H_{14}N_3]^+ Br^-$ (Figure 1b), the benzimidazole ring (mean deviation from plane 0.0080 Å) forms an angle of 10° with the γ-picoline ring (mean deviation from plane 0.0066 Å). Even if the e.s.d.'s of the bond distances (Table 1) in compound **3** are greater than in compound **2**, the trend of N-C bond lengths is in accord. In compound **4** $[C_{16}H_{16}N_3]^+ Br^-$ (Figure 2a) the N-C bond distances behave as in compound **2**.

Unlike compounds **2**-**4**, in compound **5** $[C_{17}H_{19}N_3]^{2+}[Br^-]_2•3H_2O$ (Figure 2b) the N(1,3)-C(2) bond distances are equal (1.335(5) Å av.) within the e.s.d.'s and shorter than all other N-C bonds (1.382(5) Å for N(1)-C(9) and 1.357(5) Å av. for N(1')-C(2',6')) within the heterocyclic rings and for N-aliphatic chain (1.470(6) Å av.). This behavior agrees with a delocalization of the positive charge in the N(1)-C(2)-N(3) chain and not only on N(3) atom; an opening of the C(2)-N(1)-C(9) and of the C(2)-N(3)-C(4) angles is also observed with respect to compound **4**.

A great number of intra- and inter-molecular hydrogen bonds were localized in the crystal packing of compounds **3**, **4** and **5**. They are due to the interaction with the H-acceptor Br⁻ ion [6], to the presence of positive charges and to the presence in compound **5** of three molecules of crystallization water in the asymmetric unit.

A comparison between compounds **4** and **5**, where the addition of a CH_3 group on N(3) gives rise to a positive charge on the imidazolic ring, shows a significant difference between the interplanar angles formed by the benzimidazolic and picolinic rings (19° for compound **4** against

45° for compound **5**). Such a remarkable difference may be due to the repulsion between the two positively charged sites around the nitrogen atom N(1') and along the N(1)-C(2)-N(3) chain, and also to a steric hindrance between C(13) methyl group and CH(3') group. It is also possible to conclude that in the three compounds **2**, **4** and **5** the C(2)-C(2') distance value is constant.

UV-visible studies on base **2**, on salts **3-5**, and on a wide number of similar compounds show spectra with a broad and intense maximum (λ_{max}) in the range 250-340nm.

Table 3

Spectral Parameters for Compounds **1-6**

Compound	λ max (nm)	logε	Reference
1	308	4.40	[2]
2	305	4.28	this work
3	362	4.29	this work
4	344	4.23	[2,3]
5	319	4.20	[2]
6	284	4.03	[3]

In Table 3 the spectral parameters λ_{max} and logε for compounds **1-5** and for compound **6** (Scheme 2) are listed. These spectroscopic studies showed evidence that the quaternization of picoline ring in the 2-(4-methyl-2-pyridyl)benz-X-azole determines a general bathochromic effect, in agreement with an increasing of the charge transfer nature of the band [1-3]. In Table 3 we see that mono-quaternary salts **3** and **4** show, with respect to compound **2**, a red shift and the same behavior is observed for bis-quaternary salt **5**, where both heterocyclic rings are positively charged. If the spectroscopic behavior of compounds **3-5** are compared, a hypo-hypsochromic shift is observed from **3** to **4** to **5**. Two opposite effects may be invoked: the addition of positive charges that causes a bathochromic shift due to an increasing of the charge transfer, and a variation of the planarity degree into the pyridylideneimino chromogen, that obviously, if it decreases, determines an hypsochromic shift of the absorption band. In fact, the greatest

Compound	2	3	4	5
Empirical formula	$C_{14}H_{13}N_3$	$C_{15}H_{14}BrN_3$	$C_{16}H_{16}BrN_3$	$C_{17}H_{25}Br_2N_3O_3$
Formula weight	223.27	316.20	330.22	479.21
Temperature	293(2) K	293(2) K	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system, space group	monoclinic, P2$_1$/n	monoclinic, Cc	monoclinic, P2$_1$/n	triclinic P-1
Unit cell dimensions	a = 6.575(2) Å	a = 8.2710(17) Å.	a = 9.810(2) Å	a = 7.1180(14) Å
	b = 13.829(3) Å	b = 27.712(6) Å.	b = 6.9120(10) Å	b = 11.922(2) Å
	c = 13.303(3) Å	c = 5.9990(12) Å	c = 21.065(4) Å	c = 12.605(3) Å
	β = 102.09 deg.	β = 100.51(3) deg.	β = 97.54(3) deg.	α = 73.83(3) deg.
				β = 79.93(3) deg.
				γ = 79.17(3) deg.
Volume	1182.8(5) Å^{-3}	1351.9(5) Å^{-3}	1416.0(4) Å^{-3}	1000.5(3) Å^{-3}
Z, Calculated density	4, 1.254 g/cm^{-3}	4, 1.554 g/cm^{-3}	4, 1.549 g/cm^{-3}	2, 1.591 g/cm^{-3}
Absorption coefficient	0.077 mm^{-1}	3.203 mm^{-1}	3.062 mm^{-1}	4.306 mm^{-1}
F(000)	472	644	676	488
Crystal size	0.80 x 0.82 x 0.48 mm	0.05 x 0.3 x 0.5 mm	0.05 x 0.06 x 0.80 mm	0.17 x 0.32 x 0.80 mm
Theta range for data collection	2.15 to 27.55 deg.	1.47 to 25.00 deg.	1.95 to 25.70 deg.	1.80 to 27.50 deg.
Limiting indices	-8<=h<=8, 0<=k<=18, 0<=l<=17	0<=h<=9, -32<=k<=23, -7<=l<=7	-11<=h<=11, -7<=k<=8, 0<=l<=25	-9<=h<=9, -14<=k<=15, -14<=l<=16
Reflections collected /unique	2812 / 2705 [R(int) = 0.0138]	2189 / 1269 [R(int) = 0.0255]	6637 / 2670 [R(int) = 0.0534]	9508 / 4588 [R(int) = 0.0229]
Min-max trans. factor	0.852-0.871	0.088-0.125	0.078.0.352	0.052-0.085
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints /param.	2705/0/156	1269/2/172	2670/0/182	4588/2/244
Goodness-of-fit on F^{2}2	1.036	0.872	0.900	1.024
Final R indices [I>2sigma(I)]	R1 = 0.0403, wR2 = 0.1116	R1 = 0.0452, wR2 = 0.1115	R1 = 0.0482, wR2 = 0.1154	R1 = 0.0595, wR2 = 0.1462
R indices (all data)	R1 = 0.0542, wR2 = 0.1220	R1 = 0.0783, wR2 = 0.1536	R1 = 0.1210, wR2 = 0.1441	R1 = 0.0940, wR2 = 0.1682
Extinction coefficient	0.020(3)	0.02(3)	0.0098(14)	
Largest diff. peak and hole	0.172 and -0.134 eÅ^{-3}	0.391 and -0.396 eÅ^{-3}	0.782 and -0.938 eÅ^{-3}	0.800 and -0.645 eÅ^{-3}

bathochromic effect is from **2** to **3** where the addition of a positive charge and a small deviation from planarity occur. From **3** to **4**, the hypsochromic shift is due to a further deviation from planarity while the charge is unchanged. From **4** to **5** a great deviation from planarity (45°) seems partially to compensate the bathochromic shift due to the presence of two positive charges. This hypothesis may be further confirmed, if we consider the unbridged salt **6** [7], that shows an absorption at 284 nm in the same solvent, so hypo-hypsochromically shifted with respect to counterpart salt **5**. It is reasonable to think that in salt **5** the alkyl-bridge partially prevents the distortion effects acting in salt **6** freely. In fact, an energy calculation with MOLDRAW program (see above) showed two big maxima in the energy profiles in correspondence of the two planar configurations and a flat minimum of energy for angles near 90° between the rings.

EXPERIMENTAL

All heterocyclic compounds were synthesized by literature procedures: compound **1** [8], compounds **2** and **3** [1], compounds **4** and **5** [3]. Electronic spectra were recorded in ethanol 95% with Unicam UV/vis UV2 spectrometer.

Crystals suitable for X-ray analysis were prepared in the following ways: compound **2** was dissolved at 30 °C in ethyl ether and slowly cooled to room temperature; compound **3** was dissolved in a 1:1 *N,N*-dimethylformamide/H$_2$O mixture at 80 °C and slowly cooled to room temperature; compound **4** was dissolved in acetonitrile at 60 °C and slowly cooled to room temperature; compound **5** was dissolved in 1:1 acetonitrile/ethanol (95%) solution at room temperature and partially evaporated at room temperature. Crystals of compounds **2-4** appeared light yellow in color and crystals of **5** light orange colored.

The X-ray intensities were collected at room temperature on a Siemens P4 four circle diffractometer [9]. Details on crystal data, data-collection and refinement are summarized in Table 4; an empirical absorption correction (ψ scan) was applied [10]; results however for compounds **3-5** were not satisfying because they crystallize as twins and it was necessary to use irregularly-shaped fragments of crystals.

In compound **2** the methyl groups are disordered according to the well known "star" arrangement; the unit cell of compound **5** contains three molecules of water, deriving from the solvents used for the crystallization that were not dried. The refinement was anisotropic for the non-hydrogen atoms. In the four compounds some hydrogen atoms were located in the final Fourier-difference maps and their coordinates were satisfyingly refined, other hydrogen atoms were located in the calculated positions and kept fixed; for the hydrogen atoms the isotropic temperature factor was always kept fixed. SHELXS and SHELXL programs

were used for solution and refinement of data [11]; program WINGX was used for processing final structural parameters [12].

Supplementary Material.

CIF files are deposited at CCDC with numbers 196318-196321.

REFERENCES AND NOTES

[*]   Corresponding author may be reached at Tel.: +39 11 6707505; Fax: +39 11 6707855; E-mail: domenica.marabello@unito.it

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