

2,2-Dialkyl-2*H*-benzimidazoles, the high energy tautomers of the corresponding 1,2-dialkyl-1*H*-benzimidazoles. Syntheses and their complexes with Cu(I) and Ag(I)

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Received: 28 June 2007; revised 13 September 2007

Reaction of Cu(1,2-phenylenediamine)₂(ClO₄)₂ with neat RR'=O (R = methyl and/or ethyl) gives Cu(2,2-dialkyl-2*H*-benzimidazole)ClO₄, demetallation of which by the action of aqueous ammonia yields pure 2,2-dialkyl-2*H*-benzimidazoles. These are characterised by NMR. In the X-ray crystal structure, Ag(2,2-methyl-2*H*-benzimidazole)NO₃ is found to be a spiral 1D coordination polymer where the 2*H*-benzimidazole acts as an N,N bridge between two Ag(I) centers. Although 2*H*-benzimidazoles are very unstable in the free state, they are quite stable in their Cu(I) and Ag(I) complexes. The 1,2-tautomerisation in imidazole and benzimidazole have been studied by means of transition state calculations at B3LYP/6-311+G(2d,p)* level.

Coordination chemistry of the high energy form(s) of a ligand is rare possibly because of non-accessibility of such systems. The only example that we are aware of is the carbene variant of imidazole^{1,2}. Its metal chemistry is quite old, diverse and extensive with many synthetic and catalytic applications³⁻⁶. Recently, we have described the synthesis and X-ray crystal structure of a heteroleptic copper(I) complex of a substituted 2*H*-benzimidazole⁷. 2*H*-benzimidazole (**1a**) is an energetically less stable tautomer of 1*H*-benzimidazole (**2a**) and is non-aromatic. We encountered this species in our attempt to synthesize the 1,2-phenylenediamine analogue of Curtis' macrocycle⁸. 1*H*-benzimidazole occurs as an axial ligand in naturally occurring cobalamins⁹. It is not a rare ligand in the transition metal chemistry too. But prior to our work⁷, nothing was known about the metal binding ability of 2*H*-benzimidazole. Since then, we have been investigating the synthesis, electronic structure and *d*¹⁰ metal complexes of 2,

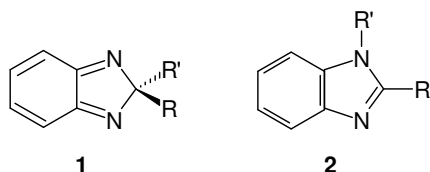
2-dialkyl substituted 2*H*-benzimidazoles. Herein we report the results. In our previous work⁷, we found that 2*H*-benzimidazole behaves as a monodentate N-donor ligand. Moreover, we show by X-ray crystallography that this unusual species can also act as a novel N,N bridging ligand, with the potential of generating coordination polymers.

Materials and Methods

All the reagents were procured commercially from Aldrich. 1,2-Phenylenediamine (OPDA) was recrystallized from 9:1 (v/v) ethanol-water mixture prior to use. Cu(OPDA)₂(ClO₄)₂ was prepared by a literature procedure¹⁰. 2,2-Dimethyl-2*H*-benzimidazole (**1b**) was synthesized by a procedure reported earlier by us⁷. Microanalyses were performed by a Perkin-Elmer 2400II elemental analyser. FTIR spectra (KBr) were recorded on a Shimadzu FTIR-8400S spectrometer, UV-vis spectra were recorded in methanol on a Perkin Elmer Lambda 950 spectrophotometer and 300 MHz NMR spectra (reference: TMS) on a Bruker DPX300 spectrometer.

Synthesis of [Ag(**1b**)]NO₃

0.17 g (1 mmol) of AgNO₃ dissolved in 30 cm³ of degassed, dehydrated methanol was added to 0.15 g (1 mmol) of 2,2-dimethyl-2*H*-benzimidazole dissolved in 20 cm³ of degassed, dehydrated methanol



a: R, R' = H b: R, R' = Me c: R, R' = Me or Et d: R, R' = Et

under dry N₂ atmosphere. Within few minutes, a yellow compound started appearing. After stirring for 2 h, the yellow compound was filtered, washed with 3 cm³ of methanol and dried *in vacuo* over fused CaCl₂. Yield, 0.21 g (65%). Single crystals suitable for X-ray analysis were grown by keeping a 5:1 (v/v) acetonitrile-water solution of the complex in a vacuum desiccator for one week. Elemental analyses were consistent with the stoichiometry C₉H₁₀N₃AgO₃ [Found: C, 34.12; H, 3.25; N, 17.22. Calc.: C, 34.18; H, 3.10; N, 17.27%]. Main FTIR bands (cm⁻¹): 3425(vb), 1625(vs), 1386(vs), 1157(m), 751(s), 582(m). ¹H NMR ((CD₃)₂SO) δ/ppm: 1.47 (s, 6H, methyl), 7.27- 7.26 (m, 4H, aromatic). ¹³C NMR ((CD₃)₂SO): δ/ppm: 22.04 (methyl), 104.62 (alkyl quaternary), 159.65 (aromatic quaternary), 125.47, 137.00 (others). UV-Vis: λ/nm (ε/dm³ mol⁻¹ cm⁻¹): 352 (1,500), 252 (36,000).

Synthesis of [Cu(1c)]ClO₄

3 g of Cu(OPDA)₂(ClO₄)₂ was suspended in 75 cm³ of ethyl methyl ketone and stirred for 10 h at room temperature. The reaction mixture gradually turned intense red. After completion of stirring, the precipitated reddish brown compound of Cu(1c)ClO₄ was filtered, washed with a few drops of ethyl methyl ketone and dried *in vacuo* over fused CaCl₂. Yield, 1.7 g (85%). Elemental analyses were consistent with the stoichiometry C₁₀H₁₂N₂CuClO₄ [Found: C, 37.34; H, 3.86; N, 8.56. Calc.: C, 37.14; H, 3.74; N, 8.67%]. Main FTIR bands (cm⁻¹): 1146(s), 1120(vs), 628(m). UV-Vis: λ/nm (ε/dm³ mol⁻¹ cm⁻¹): 420 (1,51,000), 354 (2,43,000), 278 (3,25,000), 213 (8,83,000).

Synthesis of 2-methyl-2-ethyl-2H-benzimidazole (1c)

1.2 g of Cu(1c)ClO₄ was taken in 40 cm³ of chloroform and stirred for 5 min. To the resulting dark brown suspension 25 cm³ of 30% aqueous ammonia was added and stirred for 1 h at room temperature. It was then filtered and the blue aqueous layer was discarded. The reddish brown layer was collected, evaporated at room temperature under reduced pressure to *ca.* 5 cm³ and loaded on a neutral alumina column (25 × 2.5 cm) and eluted with 1:9 (v/v) diethyl ether-petroleum ether mixture. The yellowish fraction (*ca.* 200 cm³) was collected and it was evaporated at room temperature under reduced pressure to obtain 1c as a yellowish liquid. Yield, 0.94 g (65%). Density, 1.12 g cm⁻³. Elemental analyses were consistent with the stoichiometry C₁₀H₁₂N₂ [Found: C, 74.90; H, 7.50; N, 17.42. Calc.:

C, 74.99; H, 7.35; N, 17.53%]. ¹H NMR (CDCl₃) δ/ppm: 0.62 (t, 3H, methyl of C₂H₅), 1.37 (s, 3H, methyl), 1.92 (q, 2H, methylene), 6.88-7.16 (dd, 4H, aromatic). ¹³C NMR (CDCl₃): δ/ppm: 29.01 (methylene), 8.60 (methyl C of C₂H₅), 19.67 (methyl), 106.86 (alkyl quaternary), 159.55 (aromatic quaternary), 125.46, 134.14 (others). UV-Vis: λ/nm (ε/dm³ mol⁻¹ cm⁻¹): 456 (1,300), 436 (1,300), 352 (2,000), 257 (5,200), 214 (6,200).

Synthesis of [Ag(1c)]NO₃

It was prepared in a manner similar to that used for [Ag(1b)]NO₃ by starting with 0.16 g (1 mmol) of 1c and 0.17 g (1 mmol) of AgNO₃ as a lemon yellow compound. Yield, 0.20 g (60%). Elemental analyses were consistent with the stoichiometry C₁₀H₁₂N₃AgO₃ [Found: C, 36.40; H, 3.52; N, 12.68. Calc.: C, 36.38; H, 3.66; N, 12.73%]. Main FTIR band (cm⁻¹): 1384(vs). ¹H NMR (CDCl₃) δ/ppm: 0.55 (t, 3H, methyl of C₂H₅), 1.48 (s, 3H, methyl), 2.09 (q, 2H, methylene), 7.25-7.34 (m, 4H, aromatic). ¹³C NMR (CDCl₃): δ/ppm: 29.19 (methylene), 8.50 (methyl C of C₂H₅), 20.55 (methyl), 106.91 (alkyl quaternary), 160.04 (aromatic quaternary), 125.11, 136.92 (others). UV-Vis: λ/nm (ε/dm³ mol⁻¹ cm⁻¹): 355 (1,200), 219 (3,500).

Synthesis of [Cu(1d)]ClO₄

2.5 g of Cu(OPDA)₂(ClO₄)₂ was suspended in 30 cm³ of diethyl ketone and stirred for 72 h at room temperature. Then the brown compound of Cu(1d)ClO₄ that separated from the red reaction mixture was filtered, washed with a few drops of diethyl ketone and dried *in vacuo* over fused CaCl₂. Yield, 1.36 g (77%). Elemental analyses were consistent with the stoichiometry C₁₁H₁₄N₂CuO₄ [Found: C, 39.23; H, 4.02; N, 8.27. Calc.: C, 39.16; H, 4.19; N, 8.38%]. Main FTIR bands (cm⁻¹): 1121(vs), 629(m). UV-Vis: λ/nm (ε/dm³ mol⁻¹ cm⁻¹): 359 (2,08,000), 210 (8,94,000).

Synthesis of 2,2-diethyl-2H-benzimidazole (1d)

1.2 g of Cu(1d)ClO₄ was taken in 60 cm³ of chloroform and stirred for 5 min. To the resulting dark brown suspension, 60 cm³ of 30% aqueous ammonia was added and stirred for 1 h at room temperature. It was then filtered and the blue aqueous layer was discarded. The reddish brown layer was collected, evaporated at room temperature under reduced pressure to *ca.* 5 cm³ and loaded on a neutral alumina column (25 × 2.5 cm) and eluted with

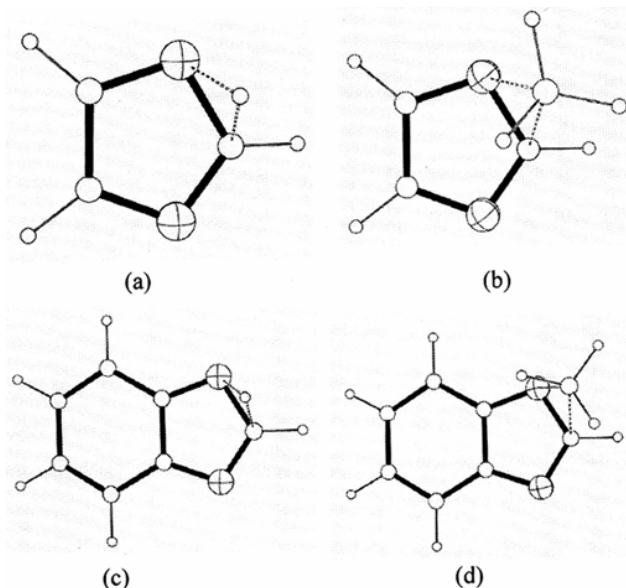
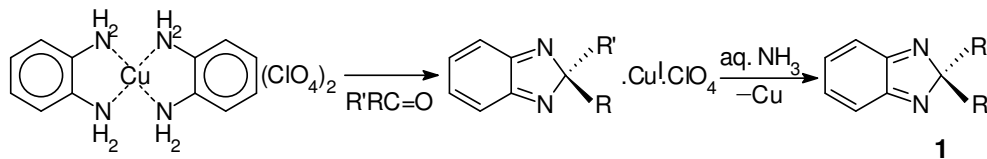


Fig. 1— Calculated transition states for (a) H migration in 1*H*-imidazole, (b) Me migration in 1*H*-1-methylimidazole, (c) H migration in **1a** and (d) Me migration in **1b**. N shown as hashed circles and C, H as open circles (Imaginary frequencies are -1489.68, -1453.19, -695.93, -677.89 cm^{-1} respectively). The dotted lines represent bonds being broken or formed. The relevant dimensions for these are (a) N-H 1.298, C-H 1.288 Å, (b) N-C 1.950, C-C 1.984 Å, (c) N-H 1.367, C-H 1.251 Å (d) N-C 1.992, C-C 1.970 Å).

3:2 (v/v) diethyl ether-petroleum ether mixture. The yellowish brown fraction (*ca.* 200 cm^3) was collected and evaporated at room temperature under reduced pressure to obtain **1d** as a yellowish solid. Yield, 0.08 g (15%). Elemental analyses were consistent with the stoichiometry $\text{C}_{11}\text{H}_{14}\text{N}_2$ [Found: C, 75.77; H, 8.01; N, 16.12. Calc.: C, 75.81; H, 8.11; N, 16.01%]. ^1H NMR δ/ppm : 1.34 (t, 3H, methyl), 1.41 (t, 3H, methyl), 2.83 (q, 2H, methylene), 4.09 (q, 2H, methylene), 7.13-7.68 (m, 4H, aromatic). ^{13}C NMR (CDCl_3): δ/ppm : 13.10 (methyl), 14.04 (methyl), 19.72 (methylene), 37.18 (methylene), 133.69, 141.70, 154.63 (quaternary), 118.04, 120.7 (others). UV-Vis: λ/nm ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$): 277 (1,28,000), 240 (14,100), 206 (36,200).

X-ray crystallography of $[\text{Ag}(\mathbf{1b})]\text{NO}_3$

The diffraction data were collected on a Nonius KappaCCD diffractometer at 110 K, using graphite monochromated $\text{MoK}\alpha$ radiation. The crystal and experimental data are summarized in Table 1. The structure was solved by Patterson methods (DIRDIF-96)¹¹, and refined by full-matrix least-squares on F^2 (SHELXL-97)¹². Intensity data were corrected for absorption effects. All non-hydrogen atoms were refined anisotropically. The hydrogens were located



Copper(II) mediated synthesis of **1**

Scheme 1

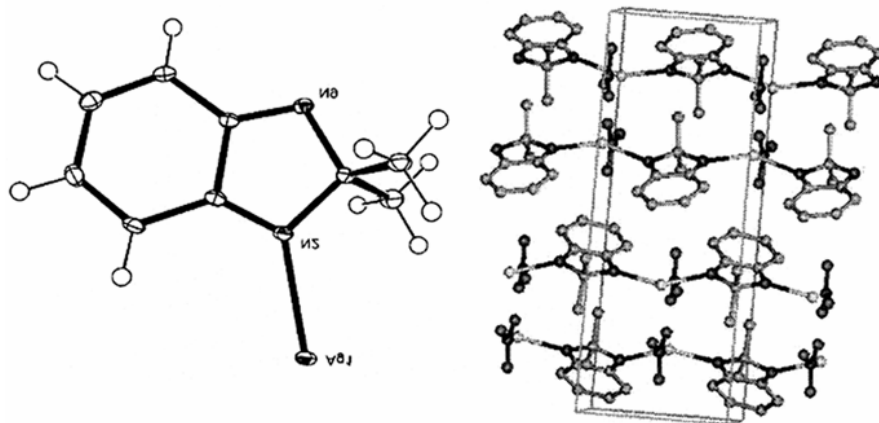


Fig. 2—Ortep view of the asymmetric unit of the cation in $\text{Ag}(\mathbf{1b})\text{NO}_3$ (left), and the arrangement of the linear coordination polymers in the crystal structure viewed down the *b*-axis (right).

in idealized positions, and were refined using a riding model with fixed thermal parameters [$U_{ij} = 1.2 U_{ij}(\text{eq})$ for the atom to which they are bonded]. The non-centrosymmetric crystal appeared to be a racemic twin.

Results and Discussion

2H-benzimidazole has an *o*-quinonoid electronic structure. Our density functional theory calculations at the B3LYP/6-311+G(2d,p)* level using Gaussian03¹³ show that in the gas phase the 2,2-dialkyl-2H-benzimidazoles (**1**) are energetically higher than the corresponding 1H-benzimidazoles (**2**) by ~ 120-145 kJ mol⁻¹ (Table 2). While there seems to be no trend, it may be noted that the difference in energy is smallest for the methyl derivatives (Table 2). The high energy difference for the R = R' = Et structures may well be due to steric repulsions between the ethyl groups in the 2H-benzimidazole.

Annular 1,3-tautomerisation in imidazole is biologically important¹⁴ as imidazole is a part of the naturally occurring amino acid histidine. The phenomenon has been extensively studied both theoretically and experimentally¹⁵⁻¹⁷. The 1, 2-tautomerisation in imidazole has not received, however, adequate attention. Our B3LYP/6-311+G(2d,p)* calculations show that the conversion of 1H-imidazole to 2H-imidazole is endothermic by 70.3 kJ mol⁻¹ with an energy barrier of 209.6 kJ mol⁻¹. The conversion is less endothermic for 1-methyl-1H-imidazole with an enthalpy of 45.2 kJ mol⁻¹ and an energy barrier of 248.2 kJ mol⁻¹. Along this trend, related studies have shown that with suitable substitutions it is even possible to have a 2H-imidazole tautomer energetically more stable than the 1H one¹⁵. In the case of unsubstituted benzimidazole, the conversion of 1H to 2H is also endothermic (by 129.9 kJ mol⁻¹) with an energy barrier of 233.8 kJ mol⁻¹. The similar conversion is less endothermic for 1-methyl-1H-benzimidazole with an enthalpy of 107.3 kJ mol⁻¹, but with a greater energy barrier (267.7 kJ mol⁻¹). The calculated structures of the transition states are shown in Fig. 1.

Earlier we had reported the copper(II) mediated synthesis of **1b** from 1,2-phenylene diamine and acetone⁷. Here we have extended the procedure to synthesise **1c** and **1d** (Scheme 1). First, the copper(I) complexes Cu(**1c**)ClO₄ and Cu(**1d**)ClO₄ have been synthesized; and then their demetallation by the action of aqueous ammonia leads to the isolation of pure 2,

Table 1— Crystallographic data for Ag(**1b**)NO₃

Empirical formula	C ₉ H ₁₀ N ₂ AgNO ₃
Formula weight	316.07
Crystal system	orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> /Å	6.6375(1)
<i>b</i> /Å	8.5291(1)
<i>c</i> /Å	17.5942(3)
<i>V</i> /Å ³	996.04(3)
<i>Z</i>	4
μ(MoKα)/mm ⁻¹	2.02
<i>D_c</i> /g.cm ⁻³	2.208
2θ _{max} /°	56.5
No. unique reflections	2383
No. reflcs. with <i>I</i> > 2σ	2322
No. refined parameters	148
<i>R</i> ₁ (<i>I</i> > 2σ)	0.018
<i>R</i> ₁ (all data)	0.019
<i>wR</i> ₂ (all data)	0.043
Flack parameter	0.44(2)
Δρ _{max} e.Å ⁻³	0.97

Table 2— Energy difference Δ*E* [= *E*(**1**) - *E*(**2**)] between some substituted 2H-benzimidazoles (**1**) and their corresponding 1H tautomers (**2**) in kJ mol⁻¹

Comp. (1)	Δ <i>E</i> (kJ mol ⁻¹)
a R, R' = H	129.9
b R, R' = Me	122.2
c R = Me, R' = Et	122.0
R = Et, R' = Me	131.2
d R = R' = Et	144.4

2-dialkyl-2H-benzimidazoles **1c** and **1d**. While **1b** and **1c** are liquid, **1d** is a solid at ambient temperature. It has been mentioned earlier that our present synthetic method for **1** is much simpler than the existing ones⁷. Earlier we could not determine the structure of the copper(I) complex Cu(**1b**)ClO₄ involved in Scheme 1. Since at times the chemistry of Cu(I) and Ag(I) are similar, we wanted to crystallize the Ag(I) complexes of preformed **1**. We have now been able to grow single crystals of Ag(**1b**)NO₃ which is prepared in good yield by reacting **1b** with AgNO₃ in dehydrated methanol in equimolar proportion. In the crystal structure, this compound forms a linear polymer of the type [Ag(**1b**)_n(NO₃)_n] (Fig. 2). The symmetry-related polymeric chains (space group *P*2₁2₁2₁) propagate parallel to the *a*-axis of the crystal. Because of geometric constraints, associated with the nitrogen donor sites being part of a five-member ring, the N-Ag-N bond angles along the polymer are significantly bent [144.10(6)°] with a slight elongation of the Ag-N(sp²) bonds [2.249(2) and 2.254(2) Å]. The metal sites are approached by the nitrate anions [Ag...N(nitrate) = 3.132(2) Å] from the concave side

of these bonds. The observed structure confirms that **1** is capable of acting as a N,N bridge between two metal centers. We believe that Cu(**1**)ClO₄ and Ag(**1c**)NO₃ have similar polymeric structure as Ag(**1b**)NO₃. It has been shown during the present investigations that although the 2*H*-benzimidazole **1** is extremely unstable, the copper(I) and silver(I) complexes of its various dialkyl derivatives reveal fair stability, the silver complex Ag(**1d**)NO₃ being the only one we failed to isolate thus far.

Supplementary Material

Supplementary crystal data for [Ag(**1b**)]NO₃ can be found in CCDC-651039 which is obtainable free of charge from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; FAX: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk.

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