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

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Reaction of Cu(1,2-phenylenediamine)\textsubscript{2}(ClO\textsubscript{4})\textsubscript{2} with neat R\textsuperscript{′}=O (R = methyl and/or ethyl) gives Cu(2,2-dialkyl-2H-benzimidazole)ClO\textsubscript{4}, demetallation of which by the action of aqueous ammonia yields pure 2,2-dialkyl-2H-benzimidazoles. These are characterised by NMR. In the X-ray crystal structure, Ag(2,2-methyl-2H-benzimidazole)NO\textsubscript{3} is found to be a spiral 1D coordination polymer where the 2H-benzimidazole acts as an N,N bridge between two Ag(I) centers. Although 2H-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\textsuperscript{1,2}. Its metal chemistry is quite old, diverse and extensive with many synthetic and catalytic applications\textsuperscript{3-6}. Recently, we have described the synthesis and X-ray crystal structure of a heteroleptic copper(I) complex of a substituted 2H-benzimidazole\textsuperscript{7}. 2H-benzimidazole (1\textsubscript{a}) is an energetically less stable tautomer of 1H-benzimi-dazole (2\textsubscript{a})\textsuperscript{7} and is non-aromatic. We encountered this species in our attempt to synthesize the 1,2-phenylenediamine analogue of Curtis’ macrocycle\textsuperscript{8}. 1H-benzimidazole occurs as an axial ligand in naturally occurring cobalamins\textsuperscript{9}. It is not a rare ligand in the transition metal chemistry too. But prior to our work\textsuperscript{7}, nothing was known about the metal binding ability of 2H-benzimidazole. Since then, we have been investigating the synthesis, electronic structure and d\textsuperscript{10} metal complexes of 2,2-dialkyl substituted 2H-benzimidazoles. Herein we report the results. In our previous work\textsuperscript{7}, we found that 2H-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)\textsubscript{2}(ClO\textsubscript{4})\textsubscript{2} was prepared by a literature procedure\textsuperscript{10}. 2,2-Dimethyl-2H-benzimidazole (1\textsubscript{b}) was synthesized by a procedure reported earlier by us\textsuperscript{7}. 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)]NO\textsubscript{3}
0.17 g (1 mmol) of AgNO\textsubscript{3} dissolved in 30 cm\textsuperscript{3} of degassed, dehydrated methanol was added to 0.15 g (1 mmol) of 2,2-dimethyl-2H-benzimidazole dissolved in 20 cm\textsuperscript{3} of degassed, dehydrated methanol

\begin{align*}
a: R, R^\prime & = H & b: R, R^\prime & = Me & c: R, R^\prime & = Me \text{ or Et} & d: R, R^\prime & = Et
\end{align*}
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 C₁₀H₁₂N₂AgO₃ [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). 

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/µm (ε/dm³ mol⁻¹ cm⁻¹): 420 (1,51,000), 354 (2,08,000), 217 (6,94,000).

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 C₂H₃), 1.37 (s, 3H, methyl), 1.92 (q, 2H, methylene), 6.88-7.16 (dd, 4H, aromatic). 

13C NMR (CDCl₃): δ/ppm: 15.16 (aliphatic quaternary), 29.19 (methylene), 8.50 (methyl C of C₂H₃), 148 (s, 3H, methyl), 2.09 (q, 2H, methylene), 7.25-7.34 (m, 4H, aromatic). Main FTIR bands (cm⁻¹): 1121(vs), 689(m). UV-Vis: λ/µm (ε/dm³ mol⁻¹ cm⁻¹): 354 (2,08,000), 217 (6,94,000).

Synthesis of [Ag(1b)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 C₁₀H₁₂N₂AgO₃ [Found: C, 36.40; H, 3.52; N, 12.68. Calc.: C, 36.38; H, 3.66; N, 12.73%]. Main FTIR bands (cm⁻¹): 1384(vs). 

1H NMR (CDCl₃) δ/ppm: 0.55 (t, 3H, methyl of C₂H₃), 1.48 (s, 3H, methyl), 2.09 (q, 2H, methylene), 7.25-7.34 (m, 4H, aromatic). Main FTIR bands (cm⁻¹): 1121(vs), 629(m). UV-Vis: λ/µm (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 C₁₁H₁₄N₄CuO₄ [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/µm (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

C, 74.99; H, 7.35; N, 17.53%].
3:2 (v/v) diethyl ether-petroleum ether mixture. The yellowish brown fraction (ca. 200 cm³) 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 C₁₁H₁₄N₂ [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). ¹³C NMR (CDCl₃): 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 (ε/dm³ mol⁻¹ cm⁻¹): 277 (1,28,000), 240 (14,100), 206 (36,200).

X-ray crystallography of [Ag(1b)NO₃]

The diffraction data were collected on a Nonius KappaCCD diffractometer at 110 K, using graphite monochromated MoKα 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 F² (SHELXL-97)¹². Intensity data were corrected for absorption effects. All non-hydrogen atoms were refined anisotropically. The hydrogens were located

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Fig. 1—Calculated transition states for (a) H migration in 1H-imidazole, (b) Me migration in 1H-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).

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Copper(II) mediated synthesis of 1

Scheme 1

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Fig. 2—Ortep view of the asymmetric unit of the cation in Ag(1b)NO₃ (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 \(U_{ij} = 1.2 U_{eq}\) 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 \(\sigma\)-quinonoid electronic structure. Our density functional theory calculations at the B3LYP/6-311+G(2d,p)* level using Gaussian03\(^{13}\) 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 important\(^{14}\) as imidazole is a part of the naturally occurring amino acid histidine. The phenomenon has been extensively studied both theoretically and experimentally\(^{15-17}\). 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 one\(^{15}\). 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 acetone\(^{2}\). Here we have extended the procedure to synthesize 1c and 1d (Scheme 1). First, the copper(I) complexes \(Cu(1c)ClO_4\) and \(Cu(1d)ClO_4\) have been synthesized; and then their demetallation by the action of aqueous ammonia leads to the isolation of pure 2, 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 ones\(^2\). Earlier we could not determine the structure of the copper(I) complex \(Cu(1b)ClO_4\) 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 \(Ag(1b)NO_3\) which is prepared in good yield by reacting 1b with AgNO\(_3\) in dehydrated methanol in equimolar proportion. In the crystal structure, this compound forms a linear polymer of the type \([Ag(1b)]_m(NO_3)_n\) (Fig. 2). The symmetry-related polymeric chains (space group \(P2_1_2_1_2\)) 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(sp\(^2\)) bonds [2.249(2) and 2.254(2) Å]. The metal sites are approached by the nitrate anions \([Ag \cdots N(nitrate) = 3.132(2) \text{ Å}\)] 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 2H−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.

References