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The synthesis of hydrophobic 1-alkyl-1*H*,1′*H*-2,2′-bibenzo[*d*]imidazoles

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Abstract: New synthesis of 1-alkyl-1*H*,1′*H*-2,2′-bibenzo[*d*]imidazoles **3** by alkylation of a disodium derivative of 1*H*,1′*H*-2,2′-bibenzo[*d*]imidazole **2a** with alkyl halides is proposed. It is noteworthy that 1,1′-dialkylated byproducts **4** are formed in yields of <5%. The structure of all obtained compounds has been confirmed by ^{1}H NMR, ^{13}C NMR, and HRMS or elemental analysis.

Keywords: 1-alkyl-1*H*,1′*H*-2,2′-bibenzo[*d*]imidazole; 1*H*,1′*H*-2,2′-bibenzo[*d*]imidazole; 2,2′-bibenzimidazole; disodium 2,2′-bibenzo[*d*]imidazole-1,1′-diide; *N*-alkylation.

Introduction

New, selective extractants have been designed for recovery of metals from primary and secondary raw materials in hydrometallurgical processes. Owing to the presence of four nitrogen atoms in 1*H*,1′*H*-2,2′-bibenzo[*d*]imidazole (**1**), this compound can form various types of complexes with *d*-electron metal ions [1–4]. The limited solubility of 1*H*,1′*H*-2,2′-bibenzo[*d*]imidazole (**1**) in commercial hydrocarbon solvents makes it impractical to use the compound as an extractant. The introduction of hydrophobic substituents into the molecule of compound **1** increases solubility and enables the use of such derivatives in the extraction stage in technological processes. Our previous studies have shown that the complexing and extracting abilities of hydrophobic derivatives of 1*H*,1′*H*-2,2′-bibenzo[*d*]imidazole (**1**) and other heterocyclic compounds (e.g. hydrophobic amides and esters of pyridinecarboxylic acids) depend on the structure, position, and number of substituents in aromatic rings. To accurately investigate the usefulness of monoalkyl- (**3**) and dialkyl-1*H*,1′*H*-2,2′-bibenzo[*d*]imidazoles (**4**) in the extraction processes, it is necessary to obtain pure compounds with well-defined structures. There are some reports in the literature describing only disubstituted derivatives of **1** as the extractants of metal ions [5]. ACORGA ZNX 50, a reagent with a bis(alkoxycarbonyl) substitution of 1*H*,1′*H*-2,2′-bibenzo[*d*]imidazole (**1**) was proposed previously as a selective extractant for zinc(II) over iron(III) from chloride solutions [6, 7].

The objective of our work was the synthesis of 1-alkyl-1*H*,1′*H*-2,2′-bibenzo[*d*]imidazoles **3**. Alkylation of disodium 2,2′-bibenzo[*d*]imidazole-1,1′-diide (**2a**) turned out to be a good method to obtain the desired compounds **3**. To the best of our knowledge, this is the first work that shows how to obtain hydrophobic mono-substituted compounds **3**. The literature describes alkylation of 1*H*,1′*H*-2,2′-bibenzo[*d*]imidazole (**1**) conducted in the presence of a base. Alkyl halides with highly hydrophobic (octadecyl) and less hydrophobic (methyl, ethyl) groups have been used to obtain 1,1′-disubstituted derivatives of 1 [8–11]. Furthermore, the reaction of compound **1** with an alkyl dihalide has been used for the synthesis of 1,1′-bridged derivatives **1** [12, 13]. The disubstituted derivatives **4** have also been obtained from 1-alkylbenzimidazoles as substrates [14–17].

There are two reports describing the preparation of 1-methyl-1*H*,1′*H*-2,2′-bibenzo[*d*]imidazole. Fieselmann and co-workers have described the synthesis of this compound by alkylation of **1** with methyl iodide in the presence of sodium methoxide. The alkylation reaction was conducted in a glass pressure vessel heated at 95°C at the pressure of 4 atm giving a mixture of both 1-methyl-1*H*,1′*H*-2,2′-bibenzo[*d*]imidazole and 1,1′-dimethyl-1*H*,1′*H*-2,2′-bibenzo[*d*]imidazole [18]. The mono-methylated derivative has also been obtained by Nguyen and co-workers by an iron sulfide-catalyzed condensation between 2-aminonitrobenzenes and 2-methylbenzimidazoles [19]. Neither of the two methods has been used to prepare more hydrophobic 1-alkyl-1*H*,1′*H*-2,2′-bibenzo[*d*]imidazoles **3**.

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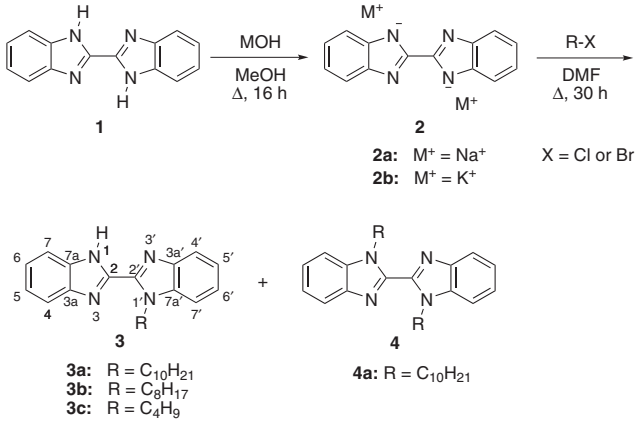
Results and discussion

1-Alkyl-1*H*,1′*H*-2,2′-bibenzo[*d*]imidazoles **3** were obtained from **1** in a two-step synthesis through the intermediary of product **2** (Scheme 1) that was generated by the reaction of **1** with sodium or potassium hydroxide. The analysis of the literature suggests that methanol is the most suitable solvent for the deprotonation reaction, and the next choices are dichloromethane, acetonitrile, or dimethylformamide (DMF) [20]. First reactions were attempted in methanol under reflux conditions. It was observed that an increase in the reaction time above 16 h (Table 1, entries 2, 3 and 8, 9) and an increase in the molar ratio of hydroxide to the substrate **1** from 2 to 4 (Table 1, entries 1–3 and 7–9, 4 and 10, 5 and 11) had no significant impact on the yield of salt **2**. Slightly lower yields of **2** are observed in cases where potassium hydroxide is used instead of sodium hydroxide (Table 1, entries 4 and 5, 10 and 11). The yields in methanol are increased with increasing the temperature (Table 1, entries 2 and 4, 8 and 10). On the other hand, the superior solubility of compound **1** in DMF results in a reduced yield because isolation of salt **2a** from the remaining starting material is difficult (Table 1, entry 6). Spectral analyses confirmed that crude salts **2a**,**b** could be used for the subsequent alkylation reaction without further purification. The ^{1}H NMR spectra of sodium salt **2a** and potassium salt **2b** indicate the absence of a singlet at 13.5 ppm assigned to the N-H protons in substrate **1**.

Alkylation of salt **2** was carried out at the reflux temperature of the reaction mixture using DMF or methanol as a solvent. When DMF was used in the alkylation reaction, 1-alkyl derivative of **1** was obtained as the main product (Table 2, entry 2) and no formation of 1,1′-dialkyl derivative of **1** was observed. Molecular modeling was used to analyze the reaction outcome. The Becke-style three-parameter density functional theory (DFT) and the Lee-Yang-Parr correlation functional B3LYP/6-31G(d,p) basis set were used to optimize molecules and compare their stability. The planar conformer s-*trans* of 1*H*,1′*H*-2,2′-bibenzo[*d*]imidazole was found to be definitely more stable (at 11.6 kcal/mol) than the nonplanar s-*cis* conformer because of the steric hindrance of (N)H atoms, causing the system to lose its planarity and resonance. The calculations showed also that 1-methyl-substituted s-*trans*-1*H*,1′*H*-2,2′-bibenzo[*d*]imidazole is a planar molecule. However, benzimidazole moieties of s-*trans* conformer of 1,1′-dimethyl-1*H*,1′*H*-2,2′-bibenzo[*d*]imidazole are not positioned in the same plane (Figure 1). One can expect that, for the extensive substituents (isobutyl, octyl, and decyl), the stability of such structures without coupling will be limited. The effective resonance-stabilization of planar s-*trans*-1-alkyl-1*H*,1′*H*-2,2′-bibenzo[*d*]imidazole is the cause of its great stability that protects it against further substitution reaction.



Scheme 1

Table 1 Synthesis of salt **2** from compound **1**.

Number	(1):MOH (mol/mol)	M	Solvent	T (°C)	Time (h)	Yield (%)
1	1:2	Na	MeOH	65	12	39
2	1:2	Na	MeOH	65	16	47
3	1:2	Na	MeOH	65	26	44
4	1:2	Na	MeOH	75	16	60
5	1:2	K	MeOH	75	16	51
6	1:2	Na	DMF	125	30	15
7	1:4	Na	MeOH	65	12	42
8	1:4	Na	MeOH	65	16	45
9	1:4	Na	MeOH	65	20	46
10	1:4	Na	MeOH	75	16	58
11	1:4	K	MeOH	75	16	52

Table 2 Synthesis of compounds **3a–c** from salt **2** and alkyl halide R-X.

Number	R	X	(2)	(2):R-X (mol/mol)	Solvent	T (°C)	Time (h)	Yield (%)
1	decyl	Cl	Na	1:2	MeOH	65	30	0
2	decyl	Cl	Na	1:2	DMF	150	30	10
3	decyl	Cl	Na	1:3	DMF	150	30	19
4	decyl	Cl	Na	1:4	DMF	150	30	61
5	decyl	Br	Na	1:4	DMF	150	30	74
6	decyl	Br	K	1:4	DMF	150	30	71
7	decyl	Cl	Na	1:4	DMF	150	40	55
8	octyl	Cl	Na	1:2	DMF	150	30	37
9	octyl	Cl	Na	1:4	DMF	150	30	76
10	octyl	Br	K	1:4	DMF	150	30	72
11	isobutyl	Br	Na	1:4	DMF	150	30	24

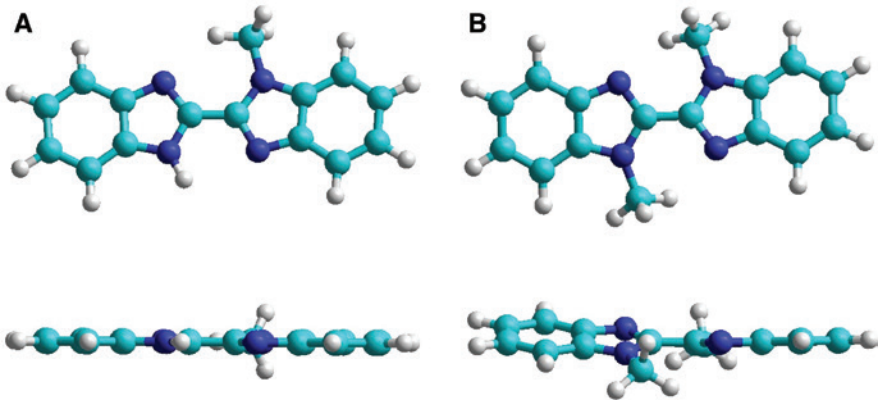


Figure 1 B3LYP/6-31G(d,p) optimized structures of the s-*trans* conformers for 1-methyl-1*H*,1′*H*-2,2′-bibenzo[*d*]imidazole (A) and 1,1′-dimethyl-1*H*,1′*H*-2,2′-bibenzo[*d*]imidazole (B).

Increasing the molar ratio of the alkyl halide to sodium salt **2a** from 2:1 to 4:1 significantly increases the yield of the formation of a monoalkyl derivative **3** (Table 2, entries 2–4, 8 and 9). On the other hand, increasing the reaction time enhances the formation of a dialkyl derivative **4**, which makes the purification of the main products **3** difficult. It is important that byproduct **4** is formed in a yield of <5%.

Byproduct **4a**, 1,1′-didecyl-1*H*,1′*H*-2,2′-bibenzo[*d*]imidazole, was isolated from the reaction mixture and its structure was confirmed by ^{1}H NMR, ^{13}C NMR, and HRMS.

Conclusion

New 1-alkyl-1*H*,1′*H*-2,2′-bibenzo[*d*]imidazoles **3a**–**c** were synthesized by alkylation of substrate **1**. The alkylation does not produce a significant amount of disubstituted byproduct **4**.

Experimental

Melting points were determined using a Boetius hot stage apparatus. The low- and high-resolution mass spectra were recorded on a Intectra Mass AMD 402 spectrometer with electron-impact ionization and 70 eV energy. The ^{1}H NMR and the ^{13}C NMR spectra were measured on a Varian Gemini 400 spectrometer (400 and 100 MHz, respectively) in $CDCl_3$, using tetramethylsilane (TMS) as an internal standard. Elemental analysis was performed on a Vario EL III (Elementar) instrument. All reagents were of analytical grade. Reaction progress and purity of the compounds were monitored by thin layer chromatography (TLC) using aluminum plates coated with silica gel (E. Merck). Silica gel 60 (E. Merck 70–230 mesh) was used for flash chromatography. Synthesis of 1*H*,1′*H*-2,2′-bibenzo[*d*]imidazole (**1**) has been described in our previous work [21].

General procedure for the synthesis of 2,2′-bibenzo[*d*]imidazole-1,1′-diide salts 2a,b

A mixture of 1*H*,1′*H*-2,2′-bibenzo[*d*]imidazole (**1**) (30 g, 0.128 mol), sodium hydroxide or potassium hydroxide (0.256 mol), and methanol (400 mL) was heated at 75°C for 16 h. After cooling, the remaining starting material was filtered off and washed with methanol. The solution was concentrated under reduced pressure and the brown-red solid residue was washed with methanol (3×50 mL) and dried at 110–120°C to give a brown-red powder of product **2a,b**.

Disodium 2,2′-bibenzo[*d*]imidazole-1,1′-diide (2a) Yield 60%; mp >350°C; ^{1}H NMR (DMSO-d_6): δ 7.28 (m, 4H, ArH), 7.64 (m, 4H, ArH); ^{13}C NMR (DMSO-d_6): δ 115.5, 122.8, 139.2, 144.0. Anal. Calcd for $C_{14}H_8N_4Na_2$: C, 60.42; H, 2.90; N, 20.14. Found: C, 60.71; H, 2.86; N, 19.98.

Dipotassium 2,2′-bibenzo[*d*]imidazole-1,1′-diide (2b) Yield 51%; mp >350°C; ^{1}H NMR (DMSO-d_6): δ 7.25 (m, 4H, ArH), 7.63 (m, 4H, ArH); ^{13}C NMR (DMSO-d_6): δ 115.5, 122.9, 139.2, 143.9. Anal. Calcd for $C_{14}H_8N_4K_2$: C, 54.17; H, 2.60; N, 18.05. Found: C, 53.92; H, 2.58; N, 18.21.

General procedure for the synthesis of 1-alkyl-1*H*,1′*H*-2,2′-bibenzo[*d*]imidazoles 3

A mixture of disodium 2,2′-bibenzo[*d*]imidazole-1,1′-diide (**2a**) (10.57 g, 0.038 mol) and DMF (150 mL) was heated under reflux until a clear solution was formed. After cooling to 80°C, the suspension was treated with decyl bromide (33.62 g, 0.152 mol) and the mixture was heated under reflux for 30 h and then concentrated. The residue was extracted with toluene. The organic phase was washed with water and dried over anhydrous magnesium sulfate. The crude product was purified by column chromatography on silica gel eluting with toluene. Pure product **3a–c** was obtained without any need for further crystallization.

1-Decyl-1*H*,1′*H*-2,2′-bibenzo[*d*]imidazole (3a) Yield 74%; mp 114–116°C; ^{1}H NMR ($CDCl_3$): δ 0.87 (t, J = 6.8 Hz, 3H, CH_3), 1.24 (s, 10H, 5×CH_2), 1.41 (m, 2H, CH_2), 1.49 (m, 2H, CH_2), 2.03 (m, 2H, CH_2), 5.14 (t, J = 7.6 Hz, 2H, NCH_2), 7.27 (m, 4H, C_5-H, C_5′-H, C_6-H and C_6′-H), 7.39 (t, J = 7.6 Hz, 1H, C_7-H), 7.55 (d, J = 8.0 Hz, 1H, C_7′-H), 7.70 (d, J = 8.4

Hz, 1H, C_4-H), 7.89 (d, *J* = 7.6 Hz, 1H, C_4′-H), 13.57 (s, 1H, NH); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.7, 26.8, 29.3, 29.3, 29.5, 29.5, 29.9, 31.9, 45.4, 110.7, 111.9, 119.5, 120.2, 122.4, 123.2, 123.9, 124.1, 134.1, 136.1, 141.9, 143.5, 143.6, 144.3; MS: *m/z* 374 (47%, M^+), 234 (100%, M^+- $C_{10}H_{20}$). HRMS. Calcd for $C_{24}H_{30}N_4$ (M^+): *m/z* 374.2470. Found: *m/z* 374.2456.

1-Octyl-1*H*,1′*H*-2,2′-bibenzo[*d*]imidazole (3b) Yield 76%; mp 85–88°C; ^{1}H NMR ($CDCl_3$): δ 0.86 (t, *J* = 7.0 Hz, 3H, CH_3), 1.26 (s, 6H, 3×CH_2), 1.40 (m, 2H, CH_2), 1.48 (m, 2H, CH_2), 2.03 (m, 2H, CH_2), 5.15 (t, *J* = 7.5 Hz, 2H, NCH_2), 7.29 (m, 4H, C_5-H, C_5′-H, C_6-H and C_6′-H), 7.40 (t, *J* = 8.0 Hz, 1H, C_7-H), 7.56 (d, *J* = 8.5 Hz, 1H, C_7′-H), 7.70 (d, *J* = 8.5 Hz, 1H, C_4-H), 7.87 (d, *J* = 8.0 Hz, 1H, C_4′-H), 13.85 (s, 1H, NH); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.6, 26.8, 29.2, 29.2, 29.9, 31.8, 45.4, 110.7, 111.9, 119.5, 120.2, 122.5, 123.2, 123.9, 124.1, 134.2, 136.1, 141.9, 143.5, 143.6, 144.3; MS: *m/z* 346 (47%, M^+), 234 (100%, M^+- C_8H_{16}). HRMS. Calcd for $C_{22}H_{26}N_4$ (M^+): *m/z* 346.2158. Found: *m/z* 346.2171.

1-Isobutyl-1*H*,1′*H*-2,2′-bibenzo[*d*]imidazole (3c) Yield 24%; mp 82–85°C; ^{1}H NMR ($CDCl_3$): δ 1.02 (d, *J* = 6.4 Hz, 6H, 2×CH_3), 2.51 (m, 1H, CH), 4.99 (d, *J* = 6.0 Hz, 2H, NCH_2), 7.25 (m, 4H, C_5-H, C_5′-H, C_6-H and C_6′-H), 7.39 (t, *J* = 6.8 Hz, 1H, C_7-H), 7.55 (d, *J* = 6.8 Hz, 1H, C_7′-H), 7.69 (d, *J* = 6.4 Hz, 1H, C_4-H), 7.89 (d, *J* = 6.4 Hz, 1H, C_4′-H), 13.84 (s, 1H, NH); ^{13}C NMR ($CDCl_3$): δ 20.2, 20.2, 29.6, 52.2, 111.1, 111.8, 119.5, 120.3, 122.5, 123.2, 123.8, 124.1, 134.0, 136.6, 141.9, 143.7, 143.7, 144.2; MS: *m/z* 290 (24%, M)$^+$, 234 (100%, M^+- C_4H_8). HRMS. Calcd for $C_{18}H_{18}N_4$ (M^+): *m/z* 290.1531. Found: *m/z* 290.1523.

1,1′-Didecyl-1*H*,1′*H*-2,2′-bibenzo[*d*]imidazole (4a) Yield 4%; mp 60–61°C; ^{1}H NMR ($CDCl_3$): δ 0.87 (t, *J* = 7.0 Hz, 6H, 2×CH_3), 1.19 (s, 16H, 8×CH_2), 1.29 (m, 12H, 6×CH_2), 1.85 (m, 4H, 2×CH_2), 4.89 (t, *J* = 7.5 Hz, 4H, 2×NCH_2), 7.36 (m, 4H, C_5-H, C_5′-H, C_6-H and C_6′-H), 7.49 (d, *J* = 7.5 Hz, 2H, C_7-H and C_7′-H), 7.86 (d, *J* = 8.0 Hz, 2H, C_4-H and C_4′-H); ^{13}C NMR ($CDCl_3$): δ 14.0, 22.6, 26.7, 29.0, 29.2, 29.4, 29.4, 29.9, 31.8, 45.4, 110.7, 120.2, 123.1, 124.2, 128.8, 135.5, 141.9; MS: *m/z* 514 (100%, M^+), 373 (97%, M^+- $C_{10}H_{21}$), 234 (70%, M^+- $C_{20}H_{40}$). HRMS. Calcd for $C_{34}H_{50}N_4$ (M^+): *m/z* 514.4011. Found: *m/z* 514.4036.

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