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# Nitro and aminobenzimidazoles

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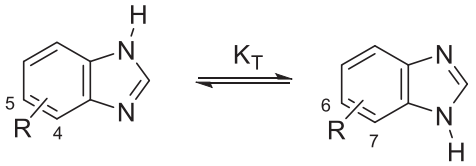
**Abstract:** A summary of the preparation methods of 2 tautomeric and 4 *N*-methylated benzimidazoles with a nitro group on the benzene ring (**1—6**) and with an amino group in the same positions (**7—12**) were summarized. Annular tautomerism of the title compounds **1—12** has been studied using $^{1}H$, $^{13}C$ and $^{15}N$ NMR spectra in liquid and solid state (CPMAS), UV spectra and quantum chemical calculations.

**Keywords:** X-Nitro-1-methylbenzimidazoles, X-amino-1-methylbenzimidazoles, NMR, preparations, annular tautomerism

## Introduction

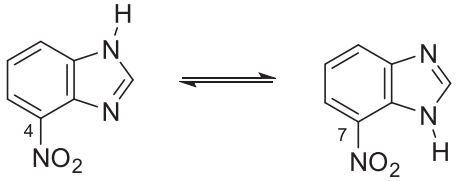
Amines are very useful starting materials for many organic syntheses of heterocycles. In case when the aminogroup on the benzene ring is attached to a heterocycle, fused quinolines are obtained (Li JJ, 2009). Their preparation is based mainly on the reduction of the corresponding nitroderivatives. Because the imidazole ring displays tautomerism, also its benzocondensed analogues with a substituent on the benzene nucleus are suitable for studying tautomerism, considering that prototropy of the imidazole nucleus can be eliminated by introducing a substituent at the nitrogen atom. Thus, a displacement of prototropic hydrogen from the imidazole ring for a methyl group eliminates the prototropy and does not significantly change chemical shifts in the $^{13}C$ NMR spectra (Fruchier et al., 1980). Therefore, benzimidazoles represent a typical annelated tautomeric system characterized by equilibrium constant $K_T$ (Elguero et al., 1976):




4(7)- or 5(6)-R-benzimidazoles

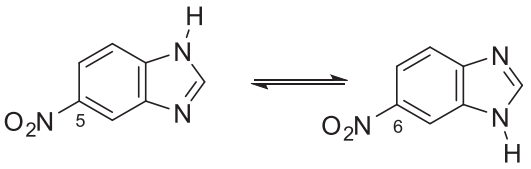
## Results and Discussion

This review is focused on the preparation of benzimidazoles with a nitro- or aminogroup on the benzene ring of benzimidazole with tautomeric hydrogen on the imidazole nucleus or their *N*-methylated homologues with eliminated tautomerism. In the first part, preparation of nitrobenzimidazoles **1—6** (Fig. 1) by: 1) nitration of the (*N*-methyl)benzimidazole derivative, 2) methylation of nitrobenzimidazole, or 3) cyclization of a suitable substituted phenylenediamine (Bella et al., 2008) is described.



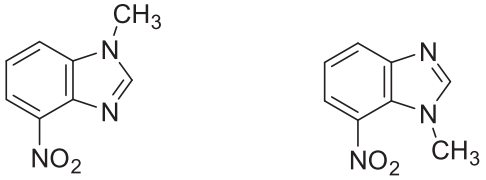

1a 1b

4-nitro-1*H*-benzimidazole 7-nitro-1*H*-benzimidazole



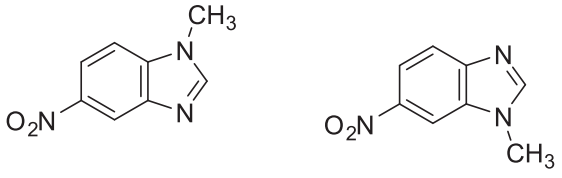

2a 2b

5-nitro-1*H*-benzimidazole 6-nitro-1*H*-benzimidazole




3 4

4-nitro-1-methylbenzimidazole 7-nitro-1-methylbenzimidazole

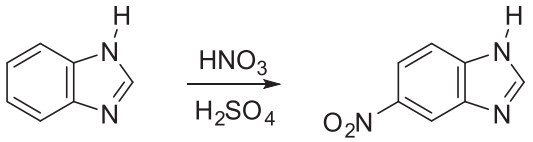



5 6

5-nitro-1-methylbenzimidazole 6-nitro-1-methylbenzimidazole

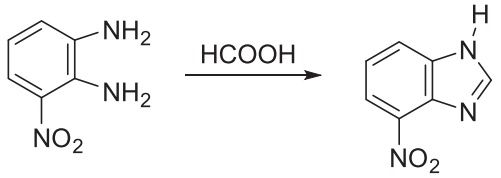
**Fig. 1.** Nitrobenzimidazoles **1—6**.

The most easily available compound is 5(6)-nitrobenzimidazole (**2**) which can be synthesized by direct nitration of benzimidazole (Zincke et al., 1896; Rabinowitz et al., 1951) like the major product accompanied with 4(7)-isomer (**1**) or one isomer from 4-nitro-1,2-phenylenediamine (Van der Want 1947):




2

The second tautomeric isomer — 4(7)-nitrobenzimidazole is accesible by cyclization of 3-nitro-1,2-phenylenediamine with formic acid (Van der Want, 1948; Rabinowitz et al., 1951):




1

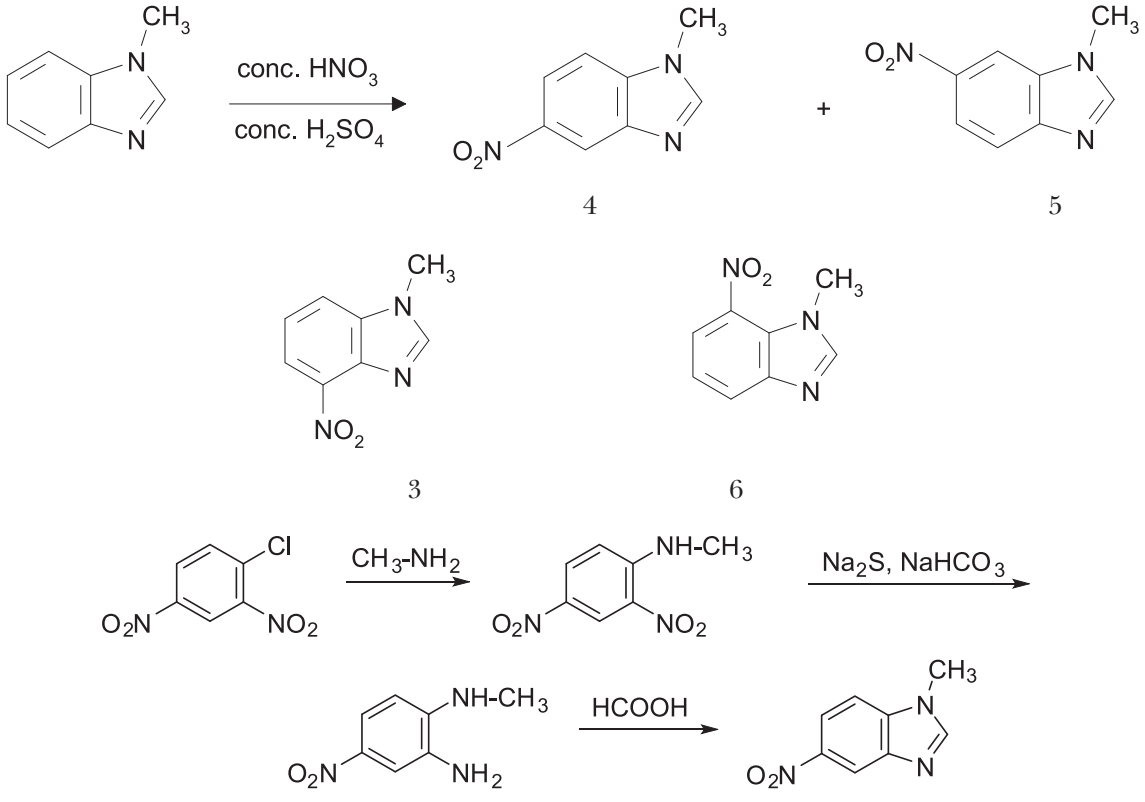
Nitration of 1-methylbenzimidazole under the conditions of benzimidazole nitration with concentrated nitric acid in concentrated sulfuric acid affords only a mixture of 5- and 6-nitro-1-methylbenzimidazoles in the ratio 49 : 51 (Milata et al., 1996):

No traces of 4- and 7-nitro-1-methylbenzimidazoles **3**, **6** were detected in the reaction mixture.

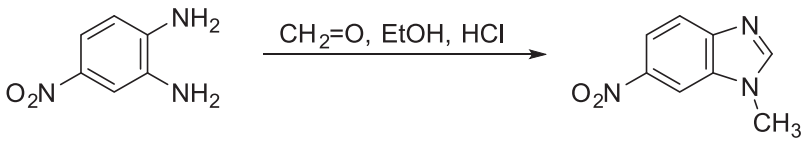
Theoretical aspects of nitration of benzazoles have been studied using the MP2/cc-pVDZ treatment (Breza et al., 2005) and it was concluded that the formation of a 5(6)-nitro-isomer can be explained formally only by the imidazole ring acting as a *meta*-orientating substituent. Benzimidazole can also exist in form of 1*H*- or 2*H*-tautomer, but the equilibrium is predominantly shifted to the 1*H*-one. Therefore, *o*-quinonoid non-aromatic species and their protonated analogues are not present. The protonated 1*H*-tautomer produces a species with an aromatic benzene ring. The protonated imidazole ring is not such a strong electron acceptor as the triazole ring (nitrated at position 4), and the aromaticity of the benzene ring is not violated.

The best available *N*-methyl isomer is 5-nitro-1-methylbenzimidazole prepared by a three-step synthesis from cheap 2,4-dinitrochlorobenzene (Joseph et al., 1962; Leandri et al., 1955):

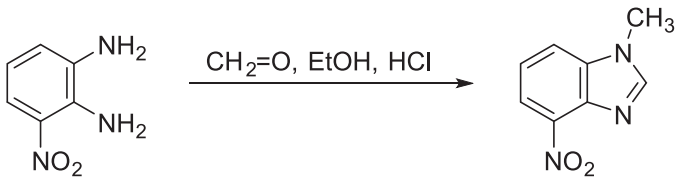
Instead of formic acid, triethyl orthoformate can be used (Ellis et al., 1974). Alkylation of 5(6)-nitrobenzimidazole described in literature as frequentioselective (Denmlow et al., 1993) lead to a mixture of 5-nitro-1-methyl- (**4**) and 6-nitro-1-methyl- (**5**) isomers, which separation is difficult (Milata et al., 1989). If other corresponding starting materials are not readily available (Leandri et al. 1955), the preparation of 6-nitro-1-methylbenzimidazole (**5**) is most




4




5




3

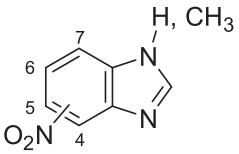
appropriately done by the reaction of 4-nitro-1,2-phenylenediamine with formaldehyde in ethanol (Ellis et al., 1974; López-Alvarado et al., 1991):

The other isomer, 5-nitro-1-methylbenzimidazole (**4**) was not found in the reaction mixture (Ellis et al., 1974). In the same way, the corresponding 3-nitro derivative resulted in 4-nitro-1-methylbenzimidazole (**3**) (Milata et al., 1993) without traces of 7-nitro-1-methylbenzimidazole (**6**):

Cyclization of 1-methyl-3-nitro-1,2-phenylenediamine prepared from hardly obtainable 2,3-dinitroaniline (Leandri et al., 1955; Reddy et al., 1979) gave the same product as obtained by fractional crystallization of the mixture of methylation products of 4(7)-nitrobenzimidazole in alkaline media (Reddy et al., 1979).

The last isomer, 7-nitro-1-methylbenzimidazole (**6**), can be prepared by a multistep reaction involving 2,6-dinitrochlorobenzene (Leandri et al. 1955; Reddy et al., 1979) or by methylation of 4(7)-nitrobenzimidazole (**1**) (Rabinowitz et al., 1951; Leandri et al., 1955; Reddy et al., 1979).

Nitrobenzimidazoles **1—6** have been subjected to regression analysis (Pappalardo et al., 1975) of the $^{1}$H NMR chemical shifts (Table 1). Equilibrium constants for the annular tautomers of two pairs of nitrobenzimidazoles (**1**, **2**) were determined and substituent effects were statistically calculated employing the $^{13}$C NMR chemical shifts (Table 2) (Fruchier et al., 1980) and UV spectra of **1—6** (Table 3) (Leandri et al., 1955). They show the influence of the substituent position on the benzene ring on the chromophore absorption:




**Tab. 1.** $^{1}$H NMR chemical shifts of X-nitrobenzimidazoles **1—6** in $CDCl_3$/acetone-$d_6$/$CF_3COOD$.

| Benzimidazole | Chemical shifts, δ ppm | | | | | |
|---|---|---|---|---|---|---|
| | H-2 | H-4 | H-5 | H-6 | H-7 | NMe |
| 4(7)-nitro | i | | i | i | i | |
| **1** | 8.45 | – | 8.06 | 7.44 | 8.17 | – |
| | 9.44 | | 8.67 | 7.99 | 8.40 | |
| 5(6)-nitro | i | i | | i | i | |
| **2** | 8.50 | 8.56 | – | 8.17 | 7.77 | – |
| | 9.50 | 8.99 | | 8.71 | 8.20 | |
| 4-nitro-1-methyl | 8.14 | | 8.17 | 7.41 | 7.73 | 3.99 |
| **3** | 8.35 | – | 8.05 | 7.43 | 7.98 | 4.02 |
| | 9.39 | | 8.67 | 7.95 | 8.34 | 4.39 |
| 5-nitro-1-methyl | 8.05 | 8.68 | | 8.24 | 7.55 | 3.90 |
| **4** | 8.30 | 8.53 | – | 8.20 | 7.68 | 4.02 |
| | 9.38 | 8.87 | | 8.65 | 8.07 | 4.33 |
| 6-nitro-1-methyl | 8.11 | 7.83 | 8.20 | | 8.37 | 3.96 |
| **5** | 8.37 | 7.78 | 8.15 | – | 8.45 | 4.07 |
| | 9.38 | 8.13 | 8.65 | | 8.87 | 4.36 |
| 7-nitro-1-methyl | 7.98 | 8.11 | 7.35 | 8.03 | | 4.09 |
| **6** | 8.27 | 8.21 | 7.37 | 8.00 | – | 4.05 |
| | 9.28 | 8.30 | 7.89 | 8.46 | | 4.44 |

Adopted from Pappalardo et al., 1975. i — insoluble.

**Tab. 2.** $^{13}C$ NMR chemical shifts of X-nitrobenzimidazoles **1—6**.

| Benzimidazole | Chemical shifts, δ ppm, in DMSO-$d_6$ | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | C-2 | C-4 | C-5 | C-6 | C-7 | C-3a | C-7a | NMe |
| 4(7)-nitro | 145.2 | 133.8[c] | 118.9 | 121.2 | 126.6[c] | 145.4[c] | 128.0[c] | - |
| 5(6)-nitro | 146.7 | 112.7 | 142.8 | 117.6 | 114.9 | 138.6 | 141.7 | - |
| 4-nitro-1-methyl | 148.2 | 138.5 | 117.4 | 121.7 | 118.3 | 136.4 | 137.4 | 31.2 |
| 5-nitro-1-methyl | 148.7 | 115.5 | 142.8[*] | 117.8 | 110.9 | 142.5[*] | 139.4 | 31.2 |
| 6-nitro-1-methyl | 149.8 | 119.6 | 117.0 | 142.8 | 107.6 | 147.8 | 134.4 | 31.2 |
| 7-nitro-1-methyl | 149.0 | 138.5 | 117.4 | 121.7 | 118.3 | 136.4 | 137.4 | 35.1 |

Adopted from Fruchier et al., 1980. [c]Broad. [*]Chemical shifts can be reversed.

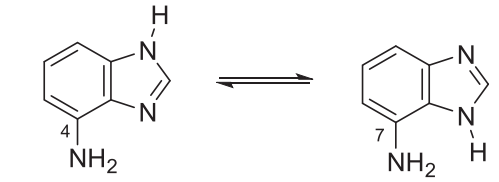
**Tab. 3.** UV spectra of nitrobenzimidazoles **1—6** in ethanol solutions.

| Compound | $\lambda_{max}$/log ε | |
|---|---|---|
| **1** | 220/3.92 | 315—318/3.93 |
| **2** | 235/4.30 | 301—303/3.97 |
| **3** | 221/3.95 | 314—319/3.90 |
| **4** | 239—240/4.34 | 303—304/3.95 |
| **5** | 238—239/4.23 | 302/4.04 |
| **6** | 225/3.79 | 313—318/3.72 |

Adopted from Leandri et al., 1955.

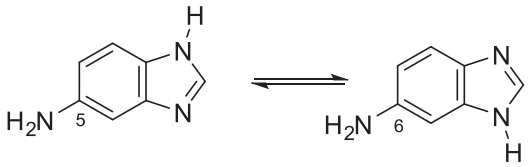
The corresponding amines **7—12** (Fig. 2) were synthesized using stannous chloride (López-Alvarado et al., 1991) or by catalytic reduction with catalysts: Adams (Ellis et al., 1974), Raney or Pd/C (Garcia et al., 2009). The synthesis of 4-amino-1-methylbenzimidazole (**9**) from 2,6-dinitroaniline or 1,2,3-triaminobenzene using rational approach has been reported recently (Van der Want, 1947; Efros, 1953; Marcos et al., 1991). 5(6)-Aminobenzimidazole (**8**) was prepared from 1,2,4-triaminobenzene upon its cyclization with formic acid (Van der Want, 1947) and 7-amino-1-methylbenzimidazole (**12**) was prepared from 2,6-dinitro-*N*-methylaniline (Efros et al., 1957). Alkylation of aminobenzimidazoles also affords mixtures of regioisomers (Howell et al., 1993; Haque et al., 1994). Basicity of the benzimidazole ring/amino group were measured (Efros, 1953) for 4(7)-aminobenzimidazole (**7**) (p$K_b$ = 8.7/12.5) and 5(6)-tautomer (**8**) (p$K_b$ = 7.4/10.7) and (Efros et al., 1957) for 7-amino-1-methylbenzimidazole (**12**) (p$K_b$ = 8.21/11.65) and 5-aminoisomer (**10**) (p$K_b$ = 7.79/11.71) (Fig. 2).

Amines and especially heterocyclic ones are readily oxidized in air which complicates their study (Lythgoe et al., 1993). 5(6)-Aminobenzimidazoles were found to form stable hydrates (Kada et al., 1974). Literature results on annular tautomerism of NH-



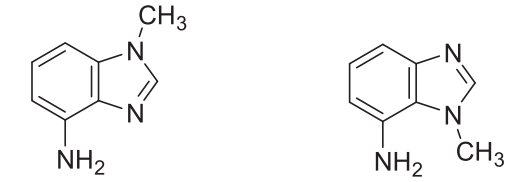
7a 7b

4-amino-1*H*-benzimidazole 7-amino-1*H*-benzimidazole



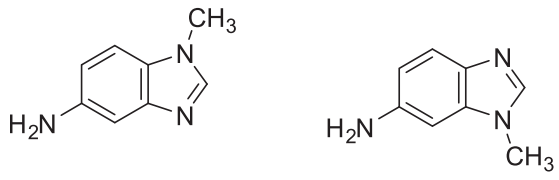
8a 8b

5-amino-1*H*-benzimidazole 6-amino-1*H*-benzimidazole



9 10

4-nitro-1-methylbenzimidazole 7-nitro-1-methylbenzimidazole



11 12

5-nitro-1-methylbenzimidazole 6-nitro-1-methylbenzimidazole

**Fig. 2.** Aminobenzimidazoles **7—12**.

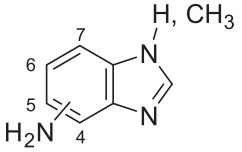
benzimidazoles are scarce. While 4(7)-aminobenzimidazole (**7**) exists in DMSO-$d_6$ (Table 4) only as the 1*H*- and not 7*H*-tautomer (also 4-amino-1*H*- and

**Tab. 4.** $^{13}C$ NMR chemical shifts of aminobenzimidazoles **7—12** in DMSO-$d_6$ (δ in ppm).

| Compound | C-2 | C-3a | C-4 | C-5 | C-6 | C-7 | C-7a | *N*-Me |
|---|---|---|---|---|---|---|---|---|
| **7a** | 138.9 | 131.9 | 139.9 | 103.9 | 123.2 | 99.3 | 133.7 | – |
| **9** | 141.5 | 132.1 | 140.1 | 104.3 | 123.4 | 97.6 | 135.2 | 30.6 |
| **10** | 144.3 | 145.4 | 109.0 | 122.2 | 108.6 | 135.3 | 124.1 | 33.2 |
| **8a** | 140.8 | ca. 145[a] | 102.5 | ca. 146[a] | 111.2 | 111.2 | ca. 127 (br)[a] | – |
| **8b** | 138.9 | 134.5 | 118.9 | 111.2 | 144.7 | 94.7 | 135.3 | – |
| **11** | 143.5 | 144.6 | 102.6 | 143.9 | 112.1 | 109.8 | 127.3 | 30.5 |
| **12** | 141.6 | 135.5 | 119.3 | 111.1 | 144.9 | 92.9 | 135.8 | 30.2 |

[a]These signals are under the signals of the most abundant tautomer.

not 7-amino-1*H*-tautomer), but in HMPA-$d_{18}$ (Table 5) as both tautomers.




4(7)-Aminobenzimidazole (**7**) was studied by a combination of theoretical (B3LYP/6-31++G**) and matrix-isolation FT-IR methods (Ramaekers et al., 2003; Houben et al., 2004). In the Ar matrix, only monomers exist. Main conclusions of the study by Garcia et al. (2009) are: i) a mixture of **7a** 78 %/**7b** 22 % ($K_T$ = 0.28, $\Delta G_{298}$ = 3.1 kJ mol$^{-1}$ is present in the matrix; ii) according to the calculations, $\Delta G_{340}$ = 15.5 kJ mol$^{-1}$ ($K_T$ = 0.004, **7a** 0.4 %/**7b** 99.6 %); iii) large difference between the experiment and calculation can be attributed to the presence of water in the matrix which, according to authors, should stabilize the minor isomer; iv) non-planarity of the amino groups was found.

**Tab. 5.** $^{13}C$ and $^{15}N$ NMR chemical shifts of aminobenzimidazoles **7** and **8** in HMPA-$d_{18}$ (δ in ppm).

| Compd. / Atom | **7a** (60 %) (300 K) | **7b** (40 %) (300 K) | **8a** (17 %) (283 K) | **8b** (83 %) (283 K) |
|---|---|---|---|---|
| C-2 | 138.4[a] | 139.4[c] | 140.2 | 138.1 |
| C-3a | 133.2 | 144.8 | 143.1 | 136.0 |
| C-4 | 141.2 | 106.8 | 103.1 | 118.7 |
| C-5 | 103.8 | 121.7 | 143.1 | 111.2 |
| C-6 | 122.9 | 105.2 | 110.2 | 146.5 |
| C-7 | 99.0 | 136.0 | 112.7 | 94.8 |
| C-7a | 134.6 | 123.6 | 126.2 | 135.1 |
| N-1 | –234.3[b] | –229.4[d] | –232.3 | –232.3 |
| N-3 | –134.0 | –141.5 | –136.4 | –136.4 |
| $NH_2$ | –328.5 | –328.5 | –324.4 | –324.4 |

[a] $^1J_{CH}$ = 203.1;
[b] $^1J_{NH}$ = 96.9;
[c] $^1J_{NH}$ = 86.6;
[d] $^1J_{NH}$ = 96.0 (Adopted from Garcia et al., 2009).

In the solid state (Tables 6 and 7), the tautomeric composition should be simpler. Only one tautomer or a 50/50 mixture of tautomers are expected; the first case being the most common one. Very rare occurrence of 33/66 trimers or 25/75 tetramers is known (Claramunt et al., 2006; Cornago et al., 2009). The results in Table 6 correspond to 4(7)-aminobenzimidazole (**7**) existing in the solid state as the 4-amino tautomer (**7a**), which is the expected result, and 5(6)-aminobenzimidazole (**8**) existing in the solid state as a 50/50 mixture of 5-aminotautomer (**8a**) and 6-amino-1*H*-tautomers (**8b**). Since the difference in energy is small, this result is not in contradiction with the calculations (see below) nor with the results obtained in a solution, however this is the **first example of benzimidazole crystallizing as a mixture of tautomers.** A search in the CSD proved that there is no example of the existence of benzimidazole tautomer pairs in crystals (Allen, 2002).

Solid-state $^{15}N$ NMR results in Table 7 are not very useful in regard to tautomerism partly because most *N*-methyl derivatives presented splitted signals due to crystal packing effects and partly because isomerism did not produce significant effects on any of the three nitrogen signals. Compound **7** showed only three signals consistent with only one tautomer. The signals of $N_1$ and $N_3$ of compound **8** are splitted and the signal at –229.8 ppm probably corresponds to **8b** and at –225.7 to **8a**.

Minimum-energy-calculated geometries at the B3LYP/6-311++G(d,p) level within the G03 package of all compounds correspond to non-planar amino groups, as it has been found by other authors for **7a** and **7b** (Houben et al., 2004). The difference is smaller and in favor of the other tautomer in case of **8**. The first difference at 298.15 K corresponds to 99.85 % of **7a** and 0.15 % of **7b**; the second one, to 28 % of **8a** and 72 % of **8b**. Garcia et al. (2009) calculated the absolute shieldings for all compounds within the GIAO approximation.

**Tab. 6.** $^{13}$C CP MAS NMR chemical shifts of aminobenzimidazoles **7—12** (δ in ppm).

| Compound | C-2 | C-3a | C-4 | C-5 | C-6 | C-7 | C-7a | *N*-Me |
|---|---|---|---|---|---|---|---|---|
| **7a** | 139.6 | 131.2[a] | 137.1[a] | 103.1 | 121.6 | 103.1 | 133.3[a] | - |
| **9** | 140.8 | 131.6[a] | 140.1[a] | 106.5 | 127.4 | 98.2 | 135.0[a] | 29.8 |
| | | | | 105.6 | 123.8 | 97.0 | | |
| | | | | 103.0 | 122.6 | 95.3 | | |
| **10** | 145.5 | 145.4[a] | 108.8 | 123.7 | 112.7 | 135.8[a] | 126.7[a] | 33.4 |
| | | | 110.5 | 121.1 | | | 124.6[a] | 32.5 |
| **8a** (50 %) | 142.0 | 142.5[a] | 99.5 | 136.7[a] | 111.2 | 119.5 | 134.0[a] | - |
| **8b** (50 %) | 140.8 | 133.0[a] | 118.7 | 112.2 | 144.7[a] | 94.6 | 136.7[a] | |
| **11** | 146.1 | 144.7[a] | 101.5 | 144.7[a] | 111.8 | 111.8 | 128.0[a] | 30.3 |
| **12** | 142.2 | 134.2[a] | 118.9 | 109.7 | 146.9[a] | 91.9 | 136.3[a] | 29.7 |

[a]NQS signals. $^{13}$C spectra were originally referenced to a glycine sample and then the chemical shifts were recalculated to $Me_4Si$ [for the carbonyl atom δ(glycine) = 176.1 ppm]. (Adopted from Garcia et al., 2009.)

**Tab. 7.** $^{15}$N CP MAS NMR chemical shifts of aminobenzimidazoles **7—12** (δ in ppm).

| Compound | $N_1$ | $N_3$ | $NH_2$ |
|---|---|---|---|
| **7a** | –217.7 | –149.9 | –323.7 |
| **9** | –229.8, –233.8 | –143.7 | –321.5 |
| **10** | –232.3 | –138.5, –141.4 | –325.3 |
| **8a** + **8b** | –229.8, –225.7 | –143.8, –149.4 | –323.4 |
| **11** | –232.0 | –142.1 | –320.5, –322.9 |
| **12** | –234.9 | –142.2 | –319.2 |

$^{15}$N spectra were referenced to $^{15}NH_4Cl$ and then converted to the nitromethane scale using the relationship: $\delta^{15}N$(nitrometh ane) = $\delta^{15}N$(ammonium chloride) – 338.1 ppm. (Adopted from Garcia et al., 2009.)

## Conclusions

In this review, an overview of ambiguous and unambiguous methods of the synthesis of tautomeric and the corresponding non-tautomeric methylated nitro- and aminobenzimidazoles with a substituent on the benzene ring is presented. Tautomerism has been studied using $^1$H, $^{13}$C and $^{15}$N NMR spectra in liquid and solid state (CP MAS technique) and compared with quantum chemical calculations. 4(7)-Nitrobenzimidazole (**1**) exists in solution in form of the dominating tautomer 7-nitro-1*H*-benzimidazole (**1b**) (85 ± 6 %) and its 5(6)-isomer (2) as the major tautomer 6-nitro-1*H*-benzimidazole (**2b**) (62 ± 2 %). While 5(6)-aminobenzimidazole (**8**) exists in a 50/50 mixture of both tautomers (**8a** : **8b**), 4(7)-isomer (**7**) exists in solid state as 4-amino-1*H*-tautomer (**7a**). In HMPA-$d_{18}$, 4- : 7-amino-1*H*-benzimidazole are present in the ratio of 60 : 40 and 5- : 6-amino-1H-benzimidazole, surprisingly, in the ratio of 17 : 83.

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## References

Bella M, Milata V (2008) J. Heterocycl. Chem. 45: 425—427.
Claramunt RM, Cornago P, Santa María MD, Torres V, Pinilla E, Torres MR, Elguero J (2006) Supramol. Chem. 18: 349—356.
Cornago P, Cabildo P, Claramunt RM, Bouissane L, Pinilla E, Torres MR, Elguero J (2009) New J. Chem. 33: 125—135. 10.1039/b812018h, CSD version 5.29, January 2008 update.
Allen FH, Acta Crystallogr. Sect. B 2002; B58: 380—388.
Allen FH, Motherwell WDS, Acta Crystallogr. Sect. B 2002; B58: 407—422.
Denmlow EV, Richter R, Zhivich AB (1993) J. Chem. Res. (S) 504—505.
Efros LS (1953) J. Gen. Chem. 23: 957—963 (translated p. 995).
Efros LS, Ionin BI (1957) J. Gen. Chem. 27: 406—411 (translated p. 459).
Elguero J, Marzin C, Katritzky AR, Linda P (1976) The Tautomerism of Heterocycles, Adv. Heterocyclic Chem., Academic Press, New York, Suppl. 1: 266—300.

Ellis GP, Jones RT (1974) J. Chem. Soc. Perkin Trans. I, 903—909.
Fruchier A, Pappalardo L, Elguero J (1980) Ann. Quim. 76: 79—84.
Garcia MÁ, Claramunt RM, Solčan T, Milata V, Alkotra I, Elguero J (2009) Magn. Reson. Chem. 47: 100—104.
Haque MR, Rasmussen M (1993) Aust. J. Chem. 47: 1523—1526.
Houben L, Ramaekers R, Adamowicz, Maes G (2004) Internet Electron. J. Mol. Des. 3: 163—181, http://www.biochempress.com.
Howell JR, Rasmussen M (1993) Aust. J. Chem. 46: 1177—1191.
Joseph L, Julca J (1962) J. Org. Chem. 27: 1101—1102.
Kada R, Jurášek A, Kováč J, Králik P (1974) Chem. Zvesti 28: 391—395.
Leandri G, Mangini A, Montanari F, Passerini R (1955) Gazz. Chim. Ital. 85: 769—814.
Li JJ (2009) Gould–Jacobs reaction. In: Name Reactions: A Collection of Detailed Mechanisms and Synthetic Applications (4th ed.). Springer-Verlag. p 263 doi: 10.1007/978-3-642-01053-8_113. ISBN 9783642010538.
López-Alvarado P, Avendaño C, Menéndez JC (1991) Heterocycles 32: 1003—1012.
Lythgoe DJ, McClenaghan I, Ramsden CA (1993) J. Heterocycl. Chem. 30: 113—117.
Marcos A, Pedregal C, Avendaño C (1991) Tetrahedron 47: 7459—7464.
Milata V, Ilavský D (1993) Org. Prep. Proc. Int. 25: 703—704.
Milata V, Ilavský D (1996) Bull. Soc. Chim. Belg., 105: 213—214.
Milata V, Ilavský D, Goljer I (1989) Coll. Czech. Chem. Commun. 54: 713—724.
Pappalardo L, Elguero J, Fruchier A (1975) An. Quim. 71: 598—602.
Rabinowitz JL, Wagner EC (1951) J. Amer. Chem. Soc. 73: 3030—3035.
Ramaekers R, Houben L, Adamowicz, Maes G (2003) Vibrat. Spectrosc. 32: 185—197.
Reddy VM, Reddy K (1979) Indian J. Chem. 17B: 357—359.
Van der Want (1947) Rec.Trav. Chim. 67: 45—51.
Zincke T, Helmert B (1896) J. Prakt. Chem. 2, 53: 91—106.