

# Nitro and aminobenzimidazoles

Viktor Milata

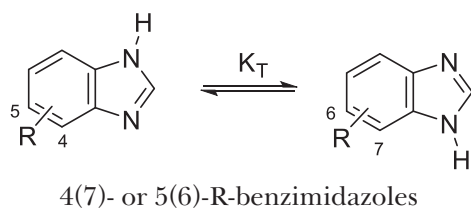
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**Abstract:** A summary of the preparation methods of 2 tautomeric and 4 *N*-methylated benzimidazoles with a nitro group on the benzene ring (**1–6**) and with an amino group in the same positions (**7–12**) were summarized. Annular tautomerism of the title compounds **1–12** has been studied using  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{15}\text{N}$  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

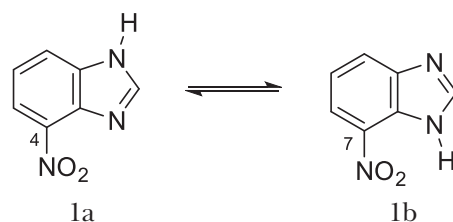
Amines are very useful starting materials for many organic syntheses of heterocycles. In case when the aminogroup on the benzene ring is attached to a heterocycle, fused quinolines are obtained (Li JJ, 2009). Their preparation is based mainly on the reduction of the corresponding nitroderivatives. Because 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  $^{13}\text{C}$  NMR spectra (Fruchier et al., 1980). Therefore, benzimidazoles represent a typical annelated tautomeric system characterized by equilibrium constant  $K_T$  (Elguero et al., 1976):



## Results and Discussion

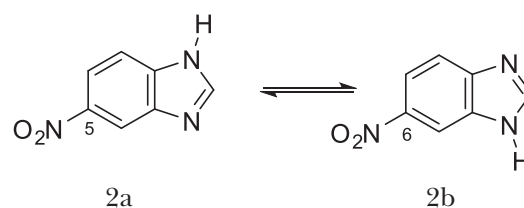
This review is focused on the preparation of benzimidazoles with a nitro- or aminogroup on the benzene ring of benzimidazole with tautomeric hydrogen on the imidazole nucleus or their *N*-methylated homologues with eliminated tautomerism. In the first part, preparation of nitrobenzimidazoles **1–6**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

tion of a suitable substituted phenylenediamine (Bella et al., 2008) is described.



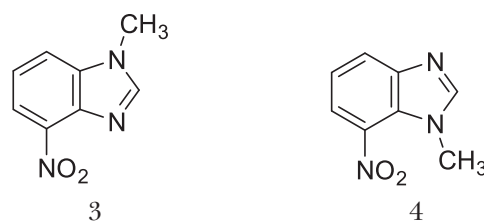
4-nitro-1*H*-benzimidazole

7-nitro-1*H*-benzimidazole



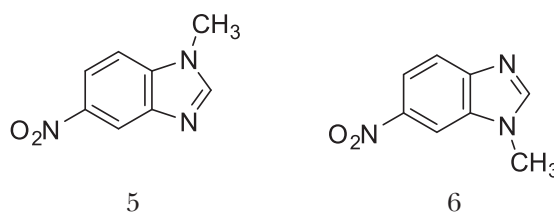
5-nitro-1*H*-benzimidazole

6-nitro-1*H*-benzimidazole



4-nitro-1-methylbenzimidazole

7-nitro-1-methylbenzimidazole

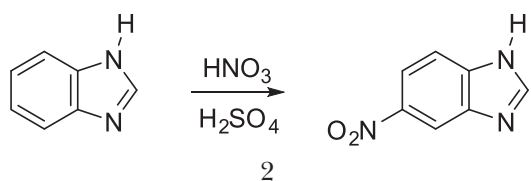


5-nitro-1-methylbenzimidazole

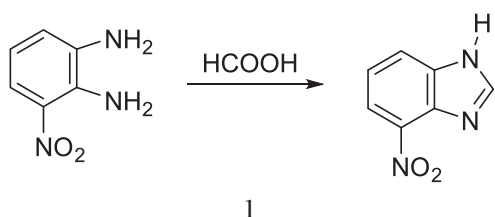
6-nitro-1-methylbenzimidazole

**Fig. 1.** Nitrobenzimidazoles **1–6**.

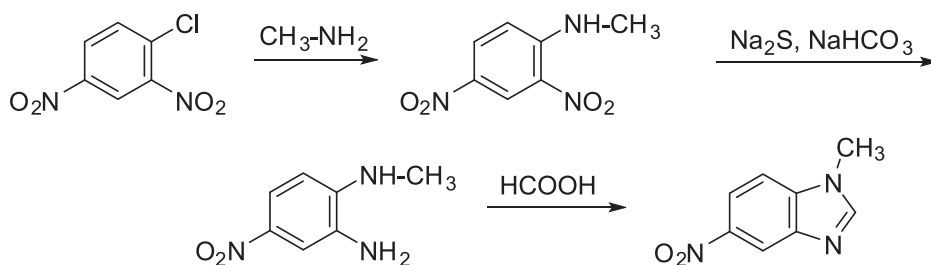
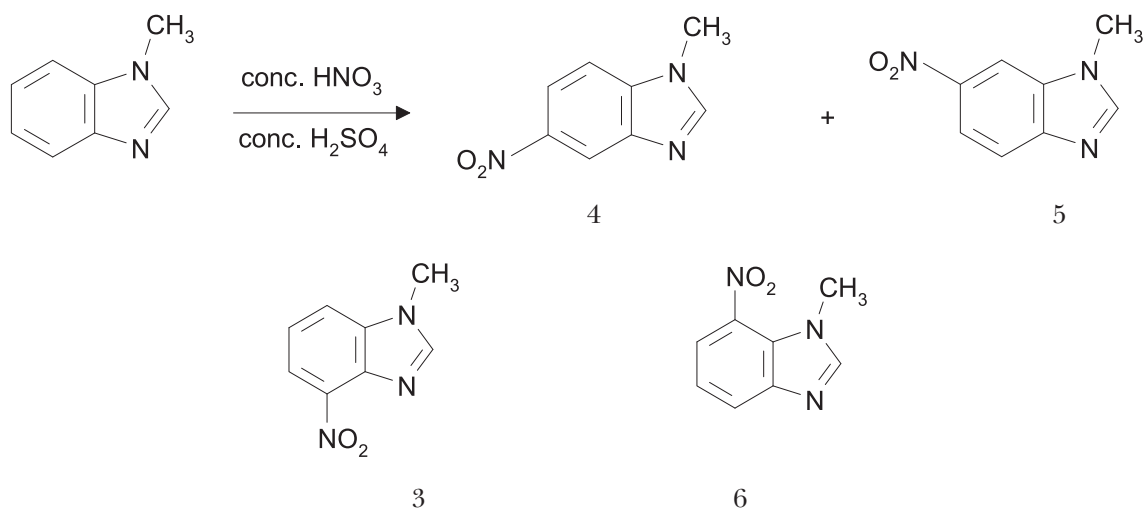
The most easily available compound is 5(6)-nitrobenzimidazole (**2**) which can be synthesized by direct nitration of benzimidazole (Zincke et al., 1896; Rabinowitz et al., 1951) like the major product accompanied with 4(7)-isomer (**1**) or one isomer from 4-nitro-1,2-phenylenediamine (Van der Want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



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



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):

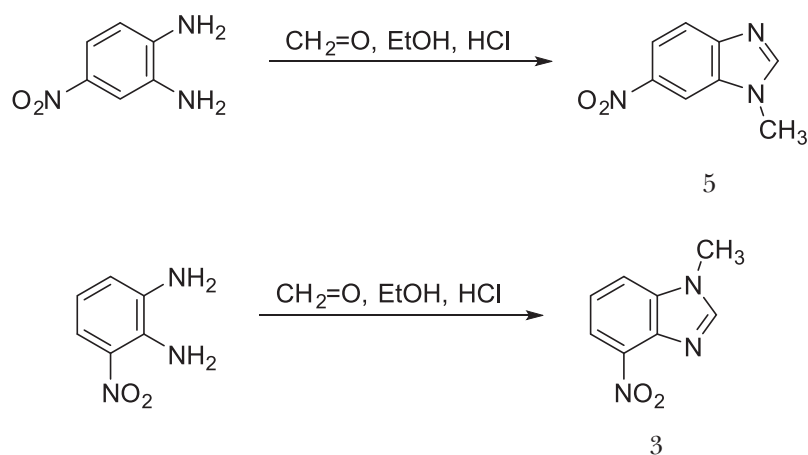


No traces of 4- and 7-nitro-1-methylbenzimidazoles **3**, **6** were detected in the reaction mixture.

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 *1H*- or *2H*-tautomer, but the equilibrium is predominantly shifted to the *1H*-one. Therefore, *o*-quinonoid non-aromatic species and their protonated analogues are not present. The protonated *1H*-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



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

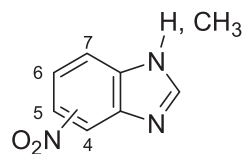
The other isomer, 5-nitro-1-methylbenzimidazole (**4**) was not found in the reaction mixture (Ellis et al., 1974). In the same way, the corresponding 3-nitro derivative resulted in 4-nitro-1-methylbenzimidazole (**3**) (Milata et al., 1993) without traces of 7-nitro-1-methylbenzimidazole (**6**):

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; Red-

dy 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  $^1\text{H}$  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  $^{13}\text{C}$  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.**  $^1\text{H}$  NMR chemical shifts of X-nitrobenzimidazoles **1–6** in  $\text{CDCl}_3/\text{acetone-}d_6/\text{CF}_3\text{COOD}$ .

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

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

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

Benzimidazole	Chemical shifts, $\delta$ 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 <sup>c</sup>	118.9	121.2	126.6 <sup>c</sup>	145.4 <sup>c</sup>	128.0 <sup>c</sup>	-
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 <sup>*</sup>	117.8	110.9	142.5 <sup>*</sup>	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. <sup>c</sup>Broad. <sup>\*</sup>Chemical shifts can be reversed.

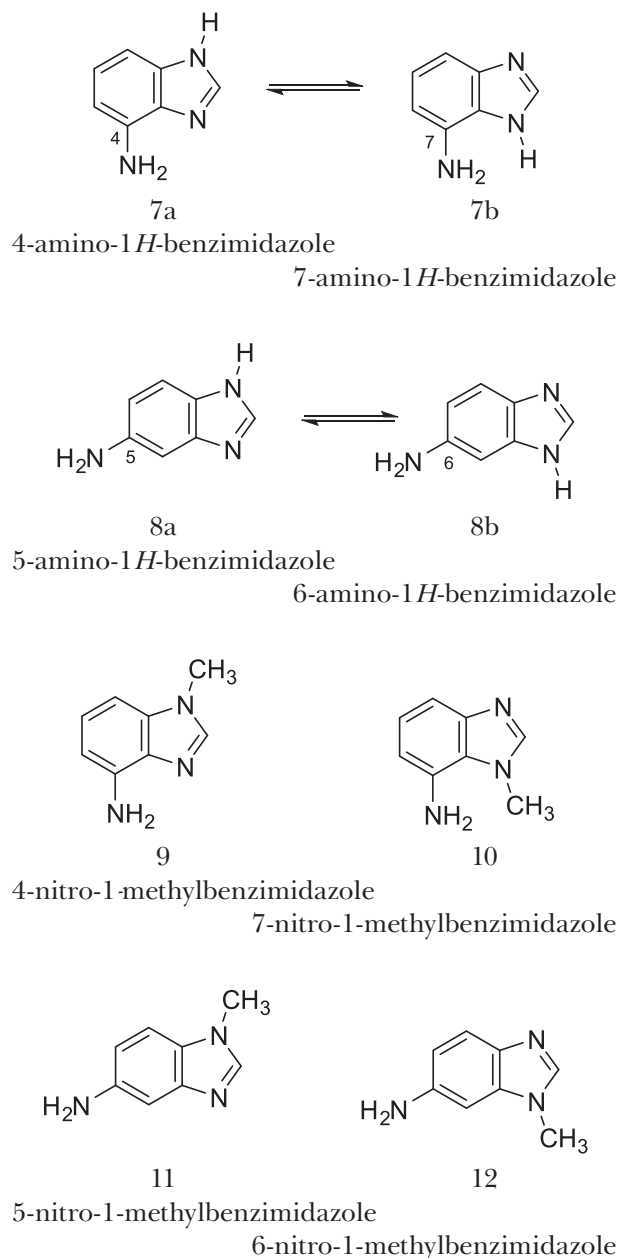
**Tab. 3.** UV spectra of nitrobenzimidazoles **1–6** in ethanol solutions.

Compound	$\lambda_{\text{max}}/\log \epsilon$	
<b>1</b>	220/3.92	315–318/3.93
<b>2</b>	235/4.30	301–303/3.97
<b>3</b>	221/3.95	314–319/3.90
<b>4</b>	239–240/4.34	303–304/3.95
<b>5</b>	238–239/4.23	302/4.04
<b>6</b>	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**) ( $\text{p}K_{\text{b}} = 8.7/12.5$ ) and 5(6)-tautomer (**8**) ( $\text{p}K_{\text{b}} = 7.4/10.7$ ) and (Efros et al., 1957) for 7-amino-1-methylbenzimidazole (**12**) ( $\text{p}K_{\text{b}} = 8.21/11.65$ ) and 5-aminoisomer (**10**) ( $\text{p}K_{\text{b}} = 7.79/11.71$ ) (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-

**Fig. 2.** Aminobenzimidazoles **7–12**.

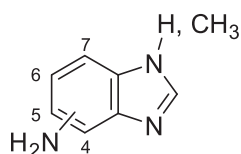
benzimidazoles are scarce. While 4(7)-aminobenzimidazole (**7**) exists in DMSO- $d_6$  (Table 4) only as the 1*H*- and not 7*H*-tautomer (also 4-amino-1*H*- and

**Tab. 4.**  $^{13}\text{C}$  NMR chemical shifts of aminobenzimidazoles **7–12** in  $\text{DMSO-d}_6$  ( $\delta$  in ppm).

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

<sup>a</sup>These signals are under the signals of the most abundant tautomer.

not 7-amino-1*H*-tautomer), but in HMPA- $\text{d}_{18}$  (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 % ( $K_T = 0.28$ ,  $\Delta G_{298} = 3.1 \text{ kJ mol}^{-1}$  is present in the matrix; ii) according to the calculations,  $\Delta G_{340} = 15.5 \text{ kJ mol}^{-1}$  ( $K_T = 0.004$ , **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,

**Tab. 5.**  $^{13}\text{C}$  and  $^{15}\text{N}$  NMR chemical shifts of aminobenzimidazoles **7** and **8** in HMPA- $\text{d}_{18}$  ( $\delta$  in ppm).

Compd.	<b>7a</b>	<b>7b</b>	<b>8a</b>	<b>8b</b>
	(60 %)	(40 %)	(17 %)	(83 %)
Atom	(300 K)	(300 K)	(283 K)	(283 K)
C-2	138.4 <sup>a</sup>	139.4 <sup>c</sup>	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 <sup>b</sup>	-229.4 <sup>d</sup>	-232.3	-232.3
N-3	-134.0	-141.5	-136.4	-136.4
NH <sub>2</sub>	-328.5	-328.5	-324.4	-324.4

<sup>a</sup> $J_{\text{CH}} = 203.1$ ;

<sup>b</sup> $J_{\text{NH}} = 96.9$ ;

<sup>c</sup> $J_{\text{NH}} = 86.6$ ;

<sup>d</sup> $J_{\text{NH}} = 96.0$  (Adopted from Garcia et al., 2009).

should stabilize the minor isomer; iv) non-planarity of the amino groups was found.

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  $^{15}\text{N}$  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  $\text{N}_1$  and  $\text{N}_3$  of compound **8** are splitted and the signal at  $-229.8 \text{ ppm}$  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.**  $^{13}\text{C}$  CP MAS NMR chemical shifts of aminobenzimidazoles **7–12** ( $\delta$  in ppm).

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

<sup>a</sup>NQS signals.  $^{13}\text{C}$  spectra were originally referenced to a glycine sample and then the chemical shifts were recalculated to  $\text{Me}_4\text{Si}$  [for the carbonyl atom  $\delta(\text{glycine}) = 176.1$  ppm]. (Adopted from Garcia et al., 2009.)

**Tab. 7.**  $^{15}\text{N}$  CP MAS NMR chemical shifts of aminobenzimidazoles **7–12** ( $\delta$  in ppm).

Compound	$\text{N}_1$	$\text{N}_3$	$\text{NH}_2$
<b>7a</b>	-217.7	-149.9	-323.7
<b>9</b>	-229.8, -233.8	-143.7	-321.5
<b>10</b>	-232.3	-138.5, -141.4	-325.3
<b>8a + 8b</b>	-229.8, -225.7	-143.8, -149.4	-323.4
<b>11</b>	-232.0	-142.1	-320.5, -322.9
<b>12</b>	-234.9	-142.2	-319.2

$^{15}\text{N}$  spectra were referenced to  $^{15}\text{NH}_4\text{Cl}$  and then converted to the nitromethane scale using the relationship:  $\delta^{15}\text{N}(\text{nitromethane}) = \delta^{15}\text{N}(\text{ammonium chloride}) - 338.1$  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  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{15}\text{N}$  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**) ( $85 \pm 6$  %) and its 5(6)-isomer (**2**) as the major tautomer 6-nitro-1*H*-benzimidazole (**2b**) ( $62 \pm 2$  %). While 5(6)-amino-benzimidazole (**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  $\text{HMPA-d}_{18}$ , 4- : 7-amino-1*H*-benzimidazole are present in the ratio of 60 : 40 and 5- : 6-amino-1*H*-benzimidazole, surprisingly, in the ratio of 17 : 83.

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