# **Investigation of Benzimidazoles**

5\*—Transmission of the Substituent Effects in 2-Substituted 5(6)-Nitrobenzimidazoles Studied by <sup>1</sup>H, <sup>13</sup>C and <sup>15</sup>N NMR Spectroscopy

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The influence of substituents on the <sup>1</sup>H, <sup>13</sup>C and <sup>15</sup>N NMR chemical shifts of 2-substituted 5(6)nitrobenzimidazoles and their analogues labelled with <sup>15</sup>N in the nitro group was investigated. It was found that the substituent effects are transmitted to the carbon and hydrogen nuclei in positions 4–7 mainly by the resonance mechanism, but to the nitro-nitrogen atom with approximately equal contributions from the resonance and inductive components. Comparison of the transmission of substituent effects in nitrobenzimidazoles with *para* and *meta* derivatives of nitrobenzene showed that the nitro group seems to be more tightly conjugated with the benzimidazole fragment than with the benzene ring.

## INTRODUCTION

Benzimidazole derivatives are widely used as biologically active compounds, herbicides and antiveiling additives in the cinema and photographic industry.<sup>2</sup> Nitrobenzimidazoles are of particular interest because of their antimicrobial activity,<sup>3</sup> and are being studied as sensitizers of hypoxic cells in the radiation therapy of cancer.<sup>4</sup>

In this work we studied the substituent influence on the  ${}^{1}H$ ,  ${}^{13}C$  and  ${}^{15}N$  NMR chemical shifts of 2-substituted 5(6)-nitrobenzimidazoles (**A** and **B**).



 $R = N(CH_3)_2, \ NH_2, \ OCH_3, \ OC_2H_5, \ CH_3, \ C_2H_5, \ H, \ Cl, \ COCH_3, \ CF_3, \ CN$ 

#### **RESULTS AND DISCUSSION**

The <sup>1</sup>H, <sup>13</sup>C and <sup>15</sup>N NMR data are given in Table 1. The presence of the nitro group in the phenylene fragment in series **A** and **B** causes non-equivalence of protons and carbons in positions 4 and 7 and of carbons in positions 5 and 6 of the benzimidazole ring as compared with their un-nitrated analogues. This gives rise to difficulty in the assignment of the <sup>1</sup>H and <sup>13</sup>C NMR signals of the nitrobenzimidazoles. The assignment of the <sup>1</sup>H and <sup>13</sup>C chemical shifts was made on the basis of previously published data<sup>5</sup> and analysis of the increments of the nitro group and chemical shifts obtained by us for benzimidazoles possessing no nitro group.<sup>6</sup>

As can be seen from Table 1, the <sup>15</sup>N and C-9 NMR signals are displaced upfield, but those of the protons and the other carbons downfield (with the exception of C-2) with an increase in electron-withdrawing properties of the substituent in position 2. The chemical shifts of the protons and carbons in positions 4 and 7 are most sensitive to the nature of the substituent.

Tables 2–5 show two-parameter correlation data for <sup>1</sup>H, <sup>13</sup>C and <sup>15</sup>N NMR chemical shifts with different sets of inductive and resonance constants of the substituents. These data indicate that the substituent effects on the chemical shifts of carbons and protons in positions 4 and 7 are mainly caused by the resonance mechanism,  $\delta$  C-4 being more sensitive to the substituent effects than  $\delta$  C-7. The contribution of the resonance component in the sum of the substituent effects at positions 5 and 6 is lower.

The substituent influence on C-8 and C-9 is also transmitted by the resonance mechanism, but low correlation coefficients for  $\delta$  C-8 do not allow one to make a reliable judgement about the contributions of the substituent effects at C-8 of the benzimidazole ring.

The  $\delta^{15}N$  correlation results with the electronic substituent parameters indicate that the substituent effects on the nitro-nitrogen atom are transmitted with approximately equal contributions from the inductive and resonance components (Tables 2–5).

The relative proportions of the effects are not very dependent on the substituent constants used. It should be noted that the correlation coefficients for  $\delta$  C-6 increase when  $\sigma_{\rm I}\sigma_{\rm R}^{0}$  constants are used.

Comparison of the data for the nitrobenzimidazoles

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<sup>\*</sup> For Part 4 see Ref. 1.

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Table 1.	<sup>1</sup> H, <sup>13</sup> C an	d <sup>15</sup> N	NMR d	chemical	shifts	of 2-sub	stituted	5(6)-nit	robenzir	nidazole	s in met	thanol (j	ppm)	
Compound <sup>a</sup>	R	H-4	H-6	H-7	H-R	C-2	C-4	C-5	C-6	C-7	C-8	C-9	C-R	<sup>15</sup> N
1	N(CH <sub>3</sub> ) <sub>2</sub>	8.014	7.952	7.225	3.307	160.00	106.90	141.80	117.49	111.58	137.57	146.02	37.55	-8.76
2	NH <sub>2</sub>	8.035	7.972	7.221	_	159.28	107.22	141.99	117.49	111.58	137.31	145.30		-8.20
3	OCH₃ <sup>b</sup>	—				162.60	109.95	142.40	117.79	113.01	137.22	143.29	57.9 <del>9</del>	
4	$OC_2H_5$	8.154	8.015	7.357	3.554 1.480	—	—	—			_		—	-9.28
5	CH₃	8.341	8.107	7.561	2.640	157.20	111.27	143.72	118.00	113.82	138.81	142.53	13.74	-9.67
6	$C_2H_5$	8.357	8.106	7.563	2.975 1.437	161.99	111.39	143.52	117.89	113.83	138.75	142.49	22.49 11.38	9.34
7	н	8.512	8.165	7.694	8.370	146.34	112.87	144.52	118.59	115.70	138.61	141.60		-9.84
8	CI	8.381	8.164	7.593			111.91	144.31	118.83	114.33	138.84	142.32		-10.65
9	COCH₃°	8.490	8.175	7.682	2.742	152.33	115.36	145.21	120.11	116.40	138.90	140.52	{191.09 25.42	-10.54
10	CF <sub>3</sub>	8.452	8.171	7.697	_	145.50	114.50	145.57	120.16	116.26	138.87	141.34	119.12	-11.34
11	CN	8.561	8.258	7.772	_	129.16	114.49	145.80	120.61	116.03	138.97	140.78	111.10	-11.71

<sup>a</sup> 1, <sup>4</sup>J(H-4, 6) = 2.5, <sup>3</sup>J(H-6, 7) = 9.2; 2, <sup>4</sup>J(H-4, 6) = 2.9, <sup>3</sup>J(H-6, 7) = 9.1; 4, <sup>4</sup>J(H-4, 6) = 2.4, <sup>3</sup>J(H-6, 7) = 8.6; 5, <sup>4</sup>J(H-4, 6) = 2.0, <sup>3</sup>J(H-6, 7) = 9.1; 6, <sup>4</sup>J(H-4, 6) = 2.4, <sup>3</sup>J(H-6, 7) = 8.7; 7, <sup>4</sup>J(H-4, 6) = 2.3, <sup>3</sup>J(H-6, 7) = 8.4; 8, <sup>4</sup>J(H-4, 6) = 2.3, <sup>3</sup>J(H-6, 7) = 8.7; 9, <sup>4</sup>J(H-4, 6) = 2.1, <sup>3</sup>J(H-6, 7) = 8.8; 10, <sup>1</sup>J(CF) = 270.6, <sup>2</sup>J(CF) = 41.2, <sup>4</sup>J(H-4, 6) = 2.2, <sup>3</sup>J(H-6, 7) = 8.8; 11, <sup>4</sup>J(H-4, 6) = 2.0, <sup>3</sup>J(H-6, 7) = 9.4.

<sup>b</sup> Signals of C-8 and C-9 are broad. <sup>c</sup> Signals of C-4, C-6 to C-9 are broad.

> Table 2. Coefficients of the correlation equation  $Y = a\sigma_I + b\sigma_R + d$  for 2-substituted 5(6)nitrobenzimidazoles SÞ Y а ь ď  $R^{a}$ n° %b<sup>d</sup> δ H-4  $0.082 \pm 0.068$  $0.487 \pm 0.039$ 0.038  $8.425 \pm 0.925$ 0.979 10 91±7 δ H-6  $0.118 \pm 0.038$  $0.223 \pm 0.023$  $8.135\pm0.901$ 0.973 0.022 75±6 10 δH-7  $0.109 \pm 0.055$  $0.493 \pm 0.032$  $7.627 \pm 0.852$ 0.986 0.031 10  $88 \pm 5$  $\Delta\delta$  C-4<sup>e</sup>  $2.96 \pm 0.86$  $6.80 \pm 0.51$  $-0.34 \pm 0.12$ 0.984 0.496 10 79±5  $2.03 \pm 0.38$  $\Delta\delta$  C-5  $3.23 \pm 0.22$  $-0.32 \pm 0.09$ 0.988 0.216 10  $72\pm4$ Δδ C-6  $3.00\pm0.59$  $1.95 \pm 0.35$  $-0.07 \pm 0.04$ 0.956 0.335 10  $51 \pm 7$ Δδ C-7  $2.09 \pm 0.59$  $4.05\pm0.35$  $-0.39 \pm 0.08$ 0.980 0.335 10 76±5 Δδ C-8  $-0.08 \pm 0.44$ 1.74±0.26  $0.19 \pm 0.05$ 0.928 0.252  $98 \pm 15$ 10 Δδ C-9  $-1.35{\pm}0.70$  $-4.32 \pm 0.41$  $0.31\pm0.09$ 0.973 0.397 10 84±7  $\delta$  <sup>15</sup>N  $-2.78 \pm 0.42$  $-1.84 \pm 0.25$  $-9.76 \pm 0.96$ 0.974 0.238 10  $52\pm5$ <sup>a</sup> Multiple correlation coefficient. <sup>b</sup> Standard error of estimate.

<sup>c</sup> Data points used.

<sup>d</sup> Contribution of resonance component.

 $^{e}\Delta\delta C = \delta C_{X} - \delta C_{H}.$ 

Y	a	 h	đ	D <sup>a</sup>	C P	n°	94 hd
		0 740 0 000	0 400 1 0 00 4	0.050	0.055		760
0 H-4	$0.067 \pm 0.098$	$0.710 \pm 0.086$	8.423±0.924	0.956	0.055	10	$92 \pm 1$
δ H-6	$0.112 \pm 0.053$	$0.324 \pm 0.046$	8.134±0.901	0.951	0.029	10	76±9
δ H-7	$0.096 \pm 0.095$	$0.716 \pm 0.083$	$7.625 \pm 0.852$	0.960	0.053	10	89±10
Δδ C-4e	$2.69 \pm 1.09$	10.08±0.96	$-0.32 \pm 0.13$	0.975	0.610	10	81±7
Δδ C-5	$1.88 \pm 0.35$	$4.86 \pm 0.31$	$-0.29 \pm 0.09$	0.990	0.198	10	74±4
Δδ C-6	$2.83 \pm 0.36$	$3.15 \pm 0.32$	$-0.01 \pm 0.03$	0.984	0.203	10	55±4
Δδ C-7	$1.89 \pm 0.58$	$6.09 \pm 0.51$	$-0.36 \pm 0.08$	0.982	0.324	10	78±5
Δδ C-8	$-0.10 \pm 0.55$	$2.50 \pm 0.48$	$0.18 \pm 0.05$	0.891	0.307	10	$96 \pm 19$
Δδ C-9	$-1.23 \pm 0.99$	$-0.27 \pm 0.87$	$0.33 \pm 0.02$	0.947	0.555	10	$85 \pm 10$
δ <sup>15</sup> N	-2.73±0.51	-2.67±0.44	-9.75±0.92	0.962	0.286	10	52±6

° Data points used.

<sup>d</sup> Contribution of resonance component.

 $^{\mathbf{e}} \Delta \delta \mathbf{C} = \delta \mathbf{C}_{\mathbf{X}} - \delta \mathbf{C}_{\mathbf{H}}.$ 

Table 4.	Coefficients of th	e correlation eq	$uation Y = a\sigma_1$	+ Dσ <sub>R</sub> + a	tor 2-su	DStitu	ted 5(0)-
	nitrobenzimidazo	les					
Y	а	b	đ	Rª	Sb	b°	%b <sup>d</sup>
δ H-4	$0.060 \pm 0.065$	$0.264 \pm 0.021$	$8.445 \pm 0.924$	0.981	0.036	10	93±7
δ H-6	$0.109 \pm 0.040$	$0.121 \pm 0.013$	$8.144 \pm 0.901$	0.971	0.022	10	77±7
δ H-7	$0.088 \pm 0.054$	$0.267 \pm 0.017$	$7.648 \pm 0.852$	0.987	0.030	10	$90 \pm 6$
$\Delta\delta$ C-4 <sup>e</sup>	2.69±1.00	$3.66 \pm 0.32$	$-0.07 \pm 0.13$	0.980	0.556	10	80±6
Δδ C-5	$1.93 \pm 0.58$	$1.71 \pm 0.18$	$-0.21 \pm 0.09$	0.972	0.323	10	73±6
Δδ C-6	$3.00 \pm 0.75$	$0.98 \pm 0.24$	$-0.04 \pm 0.03$	0.929	0.420	10	$50\pm9$
Δδ C-7	$1.95 \pm 0.74$	$2.16 \pm 0.23$	$-0.25 \pm 0.08$	0. <b>97</b> 0	0.411	10	77±7
Δδ C-8	$-0.12 \pm 0.52$	$0.92 \pm 0.16$	$0.25 \pm 0.06$	0.904	0.290	10	96±17
Δδ C-9	$-1.13 \pm 0.52$	$-2.38 \pm 0.17$	$0.10 \pm 0.09$	0.986	0.291	10	81±7
δ <sup>15</sup> N	$-2.72 \pm 0.48$	$-0.98 \pm 0.15$	$-9.82 \pm 1.14$	0.967	0.268	10	52±6
<sup>a</sup> Multiple	correlation coefficient	cient.					

<sup>b</sup> Standard error of estimate.

<sup>c</sup> Data points used.

<sup>d</sup> Contribution of resonance component.

 $^{e}\Delta\delta C = \delta C_{X} - \delta C_{H}.$ 

Table 5.	Coefficients of the benzimidazoles	correlation equa	tion $Y = a\mathcal{F} + b\mathcal{G}$	R + <b>d</b> for	2-substitu	ited 5	(6)-nitro-
Y	а	ь	đ	Rª	Sb	n°	%b <sup>d</sup>
δ H-4	$-0.008 \pm 0.066$	$0.500 \pm 0.060$	$8.427 \pm 0.924$	0.965	0.049	10	98±13
δ H-6	$0.051 \pm 0.038$	$0.222 \pm 0.034$	$8.135 \pm 0.901$	0.955	0.028	10	81±12
δ H-7	$0.010 \pm 0.063$	$0.502 \pm 0.057$	$7.628 \pm 0.852$	0.969	0.047	10	98±12
Δδ C-4 <sup>e</sup>	1.15±0.59	$6.97 \pm 0.53$	$-0.32 \pm 0.13$	0.988	0.434	10	85±6
Δδ C-5	$0.94 \pm 0.43$	$3.22 \pm 0.39$	$-0.32 \pm 0.09$	0.974	0.315	10	77±8
Δδ C-6	1.83±0.48	1.79±0.44	$-0.12 \pm 0.03$	0.949	0.358	10	49±9
Δδ C-7	$0.91 \pm 0.46$	$4.12 \pm 0.42$	$-0.39 \pm 0.08$	0.980	0.341	10	81±8
Δδ C-8	$-0.18 \pm 0.45$	1.70±0.41	$0.15 \pm 0.05$	0.868	0.337	10	$90 \pm 23$
Δδ C-9	$-0.29 \pm 0.38$	$-4.55 \pm 0.34$	$0.25 \pm 0.09$	0.987	0.277	10	94±7
δ <sup>15</sup> N	$-1.71\pm0.41$	$-1.64 \pm 0.37$	$-9.70 \pm 1.12$	0.958	0.301	10	48±8
<sup>a</sup> Multiple	correlation coeffici	ent.					

tandard error of estimate.

° Data points used.

<sup>d</sup> Contribution of resonance component.

 $^{\mathbf{e}}\Delta\delta\mathbf{C} = \delta\mathbf{C}_{\mathsf{X}} - \delta\mathbf{C}_{\mathsf{H}}.$ 

Table 6. Coefficients of the correlation equation  $\delta^{15}N = aX + bY + d$  for para- and meta-substituted nitrobenzenes

Substituent position	XY	а	ь	đ	Rª	Sb	n°	%b <sup>d</sup>	۲ <sub>12</sub> •
para-	$\sigma_{\rm i}\sigma_{\rm B}$	$-5.57 \pm 0.29$	$-0.90 \pm 0.21$	$-0.26 \pm 0.23$	0.993	0.172	9	18±4	0.328
para-	$\sigma_{\rm I}\sigma_{\rm B}^{0}$	$-5.59 \pm 0.35$	$-1.39 \pm 0.34$	$-0.27 \pm 0.25$	0.992	0.171	7	$20\pm4$	0.295
para-	$\sigma_{\rm I} \sigma_{\rm B}^+$	$-5.56 \pm 0.36$	$-0.49 \pm 0.15$	$-0.26 \pm 0.25$	0.990	0.206	9	16±4	0.360
meta-	$\sigma_{\rm I}\sigma_{\rm R}$	$-7.35 \pm 0.36$	$-1.94 \pm 0.28$	$-0.11 \pm 0.30$	0.995	0.205	8	22±3	0.333
Multiple correlation coefficient.									

<sup>b</sup> Standard error of estimate.

<sup>o</sup> Data points used: n = 9, NH<sub>2</sub>, OCH<sub>3</sub>, CH<sub>3</sub>, H, Cl, F, CF<sub>3</sub>, CN, NO<sub>2</sub>; n = 7, NH<sub>2</sub>, OCH<sub>3</sub>, CH<sub>3</sub>, H, Cl, CF<sub>3</sub>, CN; n = 8,

NH<sub>2</sub>, CH<sub>3</sub>, H, F, Br, CF<sub>3</sub>, CN, NO<sub>2</sub>.

<sup>d</sup> Contribution of resonance component.

\* Partial correlation coefficient.

with our earlier results for 2-substituted benzimidazoles possessing no nitro group,<sup>6</sup> 2-substituted 1,3perchlorates<sup>7</sup> dimethylbenzimidazolium and 2substituted 1-methylbenzimidazoles<sup>8</sup> allows us to conclude that the mechanism of the transmission of the substituent electronic effects in the systems considered is similar.

It is interesting that the resonance effect plays a more important role for positions 4 and 7 than for positions 5 and 6 of the benzimidazole ring. In this connection we compared the transmission of the substituent electronic effects by the benzimidazole ring with that by the benzene ring in para- and metasubstituted nitrobenzenes, and carried out a statistical analysis of the literature data on <sup>15</sup>N NMR spectra of para- and meta-substituted nitrobenzenes.9 The results obtained were unexpected, i.e., independently of the pairs of substituent inductive and resonance constants, the electronic effects of the substituents in both para and meta positions were transmitted to the nitronitrogen atom with an approximately 20% contribution from the resonance component (Table 6).

These data show that the nitro group in 5(6)-nitrobenzimidazole and its 2-substituted derivatives is more strongly conjugated with the benzimidazole ring than with the benzene ring in nitrobenzene and its *para* and *meta* derivatives. This suggestion does not seem to contradict the x-ray diffraction data for nitrobenzene molecules, which provide evidence for a weak nitro group-aromatic ring conjugation.<sup>10</sup>

## EXPERIMENTAL

#### 2-Substituted 5(6)-nitrobenzimidazoles

2-Substituted 5(6)-nitrobenzimidazoles (**A**) were obtained by known methods for the following R groups:  $N(CH_3)_{2,}^{11}$   $NH_{2,}^{12}$   $CH_3$  and  $H_{1,}^{13}$   $C_2H_5^{14}$   $Cl_{1,}^{15}$   $COCH_3^{16}$  and  $CF_3^{17}$ .

**2-Methoxy-5(6)-nitrobenzimidazole.** A nitrating mixture consisting of 7.6 ml of nitric acid (d = 1.42) and 11 ml of concentrated sulphuric acid at 0–5 °C was dropped on to a solution of 14.8 g (0.1 M) of 2-methoxybenz-imidazole<sup>18</sup> in 45 ml of concentrated sulphuric acid. After standing for 40 min at 0–5 °C, the reaction mixture was poured into 200 g of ice, neutralized with ammonia to pH  $\approx$  6 and the precipitate was collected. Yield 82%; m.p. 226–227 °C (from toluene or methanol). Found, C 50.04, H 3.83, N 21.82%; calculated for C<sub>8</sub>H<sub>7</sub>N<sub>3</sub>O<sub>3</sub>: C 49.74, H 3.65, N 21.75%.

**2-Ethoxy-5(6)-nitrobenzimidazole.** This was prepared analogously from 2-ethoxybenzimidazole.<sup>18</sup> Yield 87%; m.p. 152–153 °C (from toluene). Found, C 51.80, H 4.42, N 20.80%; calculated for  $C_9H_9N_3O_3$ : C 52.17, H 4.38, N 20.28%.

**2-Cyano-5(6)-nitrobenzimidazole.** A 2.8 g amount (0.01 mol) of 2-trichloromethyl-5(6)-nitrobenzimidazole<sup>19</sup> was added in batches with mixing and cooling to 15 ml of 30% aqueous ammonia. The amide of 5(6)-nitrobenzimidazole-2-carboxylic acid which precipi-

tated was filtered, and the filtrate was acidified to  $pH\approx 5$  with concentrated hydrochloric acid. The precipitate was filtered. Yield 34%; m.p. 292 °C (from methanol). Found, C 50.59, H 2.41, N 30.07%; calculated for  $C_8H_4N_4O_2$ : C 51.07, H 2.14, N 29.77%.

#### <sup>15</sup>N-enriched nitrobenzimidazoles

Nitrobenzimidazole derivatives enriched with  ${}^{15}N$  (**B**) were obtained by nitration of appropriate benzimidazoles with Na ${}^{15}NO_3$  in sulphuric acid.

#### NMR spectra

The <sup>1</sup>H NMR spectra were obtained for 0.01 M solutions on a BS-487C (Tesla, 80 MHz) NMR spectrometer and extrapolated to infinite dilution. HMDS was used as an internal standard. The <sup>1</sup>H signals were referred to Me<sub>4</sub>Si. The <sup>1</sup>H chemical shifts were determined with an accuracy of  $\pm 0.003$  ppm.

The <sup>13</sup>C NMR spectra were recorded on a Bruker WH-90 (22.68 MHz) NMR spectrometer for 0.5–1.0 M solutions under the following conditions: spectral width, 5000 Hz; data points, 8K; pulse angle in most cases, 30–45°. Cyclohexane was used as an internal standard (29.09 ppm). The <sup>13</sup>C signals were referred to Me<sub>4</sub>Si with an accuracy  $\pm 0.02$  ppm.

The <sup>15</sup>N NMR chemical shifts were obtained by the heteronuclear INDOR method, <sup>1</sup>H–(<sup>15</sup>N), on a BC-487C (Tesla, 80 MHz) spectrometer with an accuracy of  $\pm 0.02$  ppm and referred to CH<sub>3</sub>NO<sub>2</sub>.

### Statistical analysis

The statistical analysis of the results was carried out using standard programs on a BESM-6 computer. The proportion of the resonance effect was defined as described in Ref. 20. The  $\sigma_{\rm I}$ ,  $\sigma_{\rm R}$ ,  $\sigma_{\rm R}^{0}$  and  $\sigma_{\rm R}^{+}$  values were taken from Ref. 21 and  $\mathscr{F}$  and  $\mathscr{R}$  values from Ref. 20.

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