

Synthesis and reactions of both tautomers of 2-hydrazinobenzothiazole

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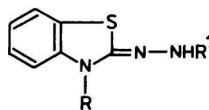
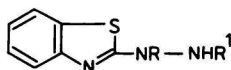
Dedicated to Professor RNDr. V. Sutoris, CSc., in honour of his 60th birthday

The structure of both 2-hydrazinobenzothiazole tautomers was proved by acetylation and formylation of 2-hydrazinobenzothiazole and 2-hydrazonobenzothiazolinone.

В работе описывается ацетилирование и формилирование 2-гидразинбензотиазола и 2-гидразонбензотиазолинона, что является синтетическим доказательством строения индивидуальных таутомеров.

Heterocyclic hydrazines were reported [1—4] to exist in two tautomeric forms — as hydrazines and hydrazones. The hydrazine form is created in acid, the hydrazone one in alkaline media. Both tautomers exist side by side in the reaction medium.

The attempted synthesis of 2-hydrazinobenzothiazole (*I*) also afforded 2-hydrazonobenzothiazolinone (*II*)

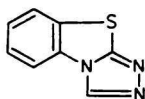


	R	R'		R	R'
<i>I</i>	H	H	<i>II</i>	H	H
<i>III</i>	H	COCH ₃	<i>IV</i>	COCH ₃	H
<i>V</i>	COCH ₃	COCH ₃	<i>VI</i>	COCH ₃	COCH ₃
<i>VII</i>	H	CHO	<i>IX</i>	CHO	H

Due to a very little solubility either in deuteriochloroform or in deuteriodimethyl sulfoxide no definite structure assignment could be attained by ¹H NMR spectroscopy. The IR spectra of both tautomers are identical as far as the position of bands is concerned; difference could be seen in the intensity of the band at $\tilde{\nu} = 1580 \text{ cm}^{-1}$, corresponding to $\nu(\text{C}=\text{N})$ in the $\text{>N}-\text{C}=\text{N}$ grouping. The higher intensity of this band of compound *I* suggests the presence of an imine form. Since these data are insufficient, both tautomers were acetylated and formylated.

Acetylation with acetic anhydride in an equivalent amount and in excess brought a decisive evidence: Acetylation of *I* and *II* with an equivalent amount of acetic anhydride in benzene furnished 2-(*N*-acetylhydrazino)benzothiazole (*III*), and 3-acetyl-2-hydrazonobenzothiazolinone (*IV*), respectively. Acetylation with an excess of acetic anhydride in the same solvent yielded 2-(*N,N'*-diacetylhydrazino)benzothiazole (*V*) and 3-acetyl-2-(*N*-acetylhydrazono)benzothiazolinone (*VI*).

Formylations were carried out with formic acid or formamide. As found, a 3 h reflux of *I* in 50 % formic acid afforded 2-(*N*-formylhydrazino)benzothiazole (*VII*), whilst formylation with an excess of formamide led to 1,2,4-triazolo-2,3-benzothiazole (*VIII*).



Compound *II* gave on formylation only 3-formyl-2-(hydrazono)benzothiazolinone (*IX*) independently on the formylation carried out by various procedures: *a*) with 50 % formic acid in excess, *b*) with concentrated formic acid in excess, *c*) with an equimolar amount of concentrated formic acid in xylene. Heating of *IX* to 80 °C for 30 min yielded *VIII*. Acetylation of *VII* with an excess of acetic anhydride led to *V*.

Experimental

2-Hydrazinobenzothiazole (*I*)

A solution consisting of 2-mercaptobenzothiazole (16.7 g; 0.1 mol) and hydrazine hydrate (30 %, 0.2 mol) in ethanol (150 cm³) was refluxed for 8 h, cooled, the yellowish compound was filtered off and crystallized from chloroform. Yield = 35 %, m.p. = 185–187 °C. For C₇H₇N₂S (*M*_r = 165.2) *w*_i(calc.): 50.88 % C, 4.26 % H, 25.43 % N, 19.40 % S; *w*_i(found): 50.57 % C, 4.19 % H, 25.19 % N, 19.33 % S. IR spectrum (nujol), $\tilde{\nu}/\text{cm}^{-1}$: 1520 δ (NH), 1580 ν (C=N), 3080 ν (NH₂).

2-Hydrazonobenzothiazolinone (*II*)

The preceding procedure was applied for preparation of *II* with the difference that 70 % hydrazine hydrate (0.5 mol) was used. The white crystals recrystallized from ethanol had m.p. = 200–201 °C, the crude white crystals (yield = 85 %) had m.p. = 200–202 °C. For C₇H₇N₂S (*M*_r = 165.2) *w*_i(calc.): 50.88 % C, 4.26 % H, 25.43 % N, 19.40 % S; *w*_i(found):

50.74 % C, 4.22 % H, 25.00 % N, 19.32 % S. IR spectrum (nujol), $\bar{\nu}/\text{cm}^{-1}$: 1520 $\delta(\text{NH})$, 1580 $\nu(\text{C}=\text{N})$, 3080 $\nu(\text{NH}_2)$.

2-(*N*-Acetylhydrazino)benzothiazole (III)

2-Hydrazinobenzothiazole (3.6 g; 25 mmol) dissolved in benzene (70 cm^3) was refluxed with acetic anhydride (2.5 g; 250 mmol) for 5 h. The white precipitate separating after cooling was filtered off and crystallized from benzene. Yield = 85 %, m.p. = 98—100 °C. For $\text{C}_{11}\text{H}_{13}\text{N}_3\text{O}_3\text{S}$ ($M_r = 267.3$) $w_i(\text{calc.})$: 49.43 % C, 4.90 % H, 15.72 % N, 11.99 % S; $w_i(\text{found})$: 49.27 % C, 4.83 % H, 15.59 % N, 12.09 % S. ^1H NMR spectrum (deuteriochloroform, hexadeuteriodimethyl sulfoxide), δ/ppm : 2.15 (s, 3H, CH_3CO), 7.2—7.9 (m, 4H, Ar—H). IR spectrum (nujol), $\bar{\nu}/\text{cm}^{-1}$: 1520 $\delta(\text{NH})$, 1580 $\nu(\text{C}=\text{N})$, 1680 $\nu(\text{C}=\text{O})$, 2660 $\nu(\text{NH})_{\text{assoc}}$, 1760 $\nu(\text{C}-\text{O})$.

3-Acetyl-2-hydrazonobenzothiazolinone (IV)

The title product was prepared from 2-hydrazonobenzothiazolinone according to procedure described with III. Yield = 73 %, m.p. = 136—139 °C (ethanol). For $\text{C}_{11}\text{H}_{13}\text{N}_3\text{O}_3\text{S}$ ($M_r = 267.3$) $w_i(\text{calc.})$: 49.43 % C, 4.90 % H, 15.72 % N, 11.99 % S; $w_i(\text{found})$: 49.32 % C, 4.81 % H, 15.66 % N, 12.11 % S. ^1H NMR spectrum (hexadeuteriodimethyl sulfoxide), δ/ppm : 2.15 (s, 3H, CH_3CO), 2.3 (s, 3H, CH_3CO), 7.2—7.85 (m, 4H, Ar—H). IR spectrum (nujol), $\bar{\nu}/\text{cm}^{-1}$: 1310 $\nu(\text{C}=\text{N})$, 1520 $\delta(\text{NH})$, 1570 $\nu(\text{C}=\text{N})$, 1690 $\nu(\text{C}=\text{O})$, 1770 $\nu(\text{C}-\text{O})$.

2-(*N,N'*-Diacetylhydrazino)benzothiazole (V)

a) 2-Hydrazinobenzothiazole (3.6 g; 25 mmol) and acetic anhydride (10 cm^3) were refluxed with benzene (30 cm^3) for 6 h, the mixture was cooled and poured into ice-cold water. The separated crystals were filtered and crystallized from methanol. Yield = 73 %, m.p. = 183—185 °C. For $\text{C}_{11}\text{H}_{11}\text{N}_3\text{O}_2\text{S}$ ($M_r = 249.3$) $w_i(\text{calc.})$: 52.99 % C, 4.44 % H, 16.85 % N, 12.86 % S; $w_i(\text{found})$: 52.84 % C, 4.42 % H, 16.68 % N, 12.68 % S. ^1H NMR spectrum (hexadeuteriodimethyl sulfoxide), δ/ppm : 2.3 (s, 6H, CH_3CO), 7.28—8.05 (m, 4H, Ar—H). IR spectrum (nujol), $\bar{\nu}/\text{cm}^{-1}$: 1525 $\delta(\text{NH})$, 1580 $\nu(\text{C}=\text{N})$, 1690 $\nu(\text{C}=\text{O})$, 2670 $\nu(\text{NH})_{\text{assoc}}$, 1320 $\nu(\text{C}-\text{N})$.

b) 2-(*N*-Formylhydrazino)benzothiazole (3.8 g; 25 mmol) was refluxed with acetic anhydride (30 cm^3) for 5 h, the mixture was cooled and poured into ice-cold water. The separated crystals were filtered and recrystallized from methanol. Yield = 83 %, m.p. = 183—185 °C. ^1H NMR spectrum (hexadeuteriodimethyl sulfoxide), δ/ppm : 2.3 (s, 6H, CH_3CO), 7.27—8.02 (m, 4H, Ar—H).

2-(*N*-Formylhydrazino)benzothiazole (VII)

2-Hydrazinobenzothiazole (3.6 g; 25 mmol) was refluxed with 50 % formic acid (30 cm^3) for 3 h and the white crystals were recrystallized from acetone or ethanol. Yield = 75 %, m.p. = 237 °C. For $\text{C}_8\text{H}_7\text{N}_3\text{OS}$ ($M_r = 193.2$) $w_i(\text{calc.})$: 49.72 % C, 3.36 % H, 21.74 % N,

15.59 % S; $w_i(\text{found})$: 50.05 % C, 3.56 % H, 21.78 % N, 16.33 % S. ^1H NMR spectrum (hexadeuteriodimethyl sulfoxide), δ/ppm : 7.2—8.2 (m, 4H, Ar—H), 9.5 (s, 1H, CHO). IR spectrum (nujol), $\tilde{\nu}/\text{cm}^{-1}$: 1520 $\delta(\text{NH})$, 1580 $\nu(\text{C}=\text{N})$, 1690 $\nu(\text{C}=\text{O})$, 2680 $\nu(\text{NH})_{\text{assoc}}$.

1,2,4-Triazolo-2,3-benzothiazole (VIII)

2-Hydrazinobenzothiazole (3.6 g; 25 mmol) was refluxed in formamide (20 cm^3) for 2 h, the white crystals were separated and recrystallized from benzene. Yield = 63 %, m.p. = 175—177 °C. For $\text{C}_8\text{H}_5\text{N}_3\text{S}$ ($M_r = 175.2$) $w_i(\text{calc.})$: 54.84 % C, 2.87 % H, 23.98 % N, 18.30 % S; $w_i(\text{found})$: 54.74 % C, 2.74 % H, 23.76 % N, 18.18 % S. ^1H NMR spectrum (hexadeuteriodimethyl sulfoxide), δ/ppm : 6.85—7.72 (m, 4H, Ar—H), 8.12 (s, 1H, CH). IR spectrum (nujol), $\tilde{\nu}/\text{cm}^{-1}$: 1580 $\nu(\text{C}=\text{N})$, 1310 $\nu(\text{C}-\text{N})$.

3-Formyl-2-hydrazinobenzothiazolinone (IX)

a) 2-Hydrazinobenzothiazole (3.6 g; 25 mmol) was refluxed with 50 % formic acid (30 cm^3) for 3 h, the separated crystals were filtered and recrystallized from ethanol or acetone. Yield = 75 %, m.p. = 145—147 °C.

b) The same procedure was carried out with concentrated formic acid (20 cm^3) at a 30 min reflux time. Yield = 74 %.

c) The starting product was formylated with concentrated formic acid (1.3 g; 25 mmol) in refluxing xylene (50 cm^3) for 1 h. Yield = 78 %. For $\text{C}_8\text{H}_7\text{N}_3\text{OS}$ ($M_r = 193.2$) $w_i(\text{calc.})$: 49.72 % C, 3.65 % H, 21.74 % N, 16.59 % S; $w_i(\text{found})$: 49.81 % C, 3.65 % H, 21.74 % N, 16.40 % S. ^1H NMR spectrum (hexadeuteriodimethyl sulfoxide), δ/ppm : 7.25—8.20 (m, 4H, Ar—H), 9.55 (s, 1H, CHO). IR spectrum (nujol), $\tilde{\nu}/\text{cm}^{-1}$: 1520 $\delta(\text{NH})$, 1580 $\nu(\text{C}=\text{N})$, 1690 $\nu(\text{C}=\text{O})$, 2680 $\nu(\text{NH})_{\text{assoc}}$.

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