Synthesis and structure of azomethines based on *N*-vinyl derivatives of 2-amino- and 2-formylimidazoles

L. V. Baikalova, A. V. Afonin, and E. S. Domnina*

Irkutsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, 1 ul. Favorskogo, 664033 Irkutsk, Russian Federation. Fax: 007 (395 2) 35 6046

New Schiff's bases of the *N*-vinylimidazole and *N*-vinylbenzimidazole series were synthesized. ^{1}H NMR data suggest that the azomethines exist in the *E*-form with respect to the CH=N bond and that the vinyl groups have *trans*-orientation relative to each other.

Key words: *N*-vinylimidazoles, Schiff's bases, CH...N specific intramolecular interaction; ^{1}H NMR spectra.

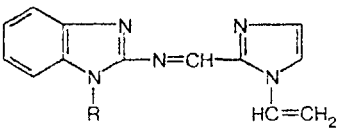
Studies of polydentate functional derivatives of 1-vinylimidazoles by ^{1}H and ^{13}C NMR spectroscopy revealed the structure and coordination centers involved in the complex formation of these ligands with metals.[1—4] In the present work, we synthesized new azomethines by the reaction of 2-aminobenzimidazole and its 1-vinyl derivative with 1-vinylimidazole(benzimidazole)-2-carbaldehydes and studied their structure using ^{1}H NMR spectroscopy.

Results and Discussion

The reactions of 1-vinylimidazole-2-carbaldehyde (**1**) and 1-vinylbenzimidazole-2-carbaldehyde (**2**) with 2-aminobenzimidazole (**3**) and 2-amino-1-vinylbenzimidazole (**4**) gave hitherto unknown azomethines **5**—**7**.

The yields of azomethines are from 10 to 30% in the presence of bases (KOH) and acids (HCl, AcOH), whereas they reach 65—75% in non-catalyzed reactions. Azomethines **5**—**7** are bright-yellow crystalline compounds, well soluble in Me_2CO and MeCN, and azomethines **6** and **7** are soluble in EtOH and C_6H_6 as well. All azomethines **5**—**7** are insoluble in H_2O and poorly soluble in Et_2O.

The structures of the compounds obtained, **5**—**7**, were established by comparing their ^{1}H NMR spectra



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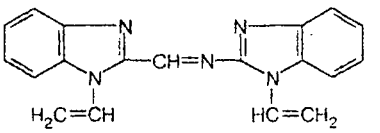
5: R = H
6: R = CH=CH$_2$



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with those of 1-vinylimidazoles and -benzimidazoles thoroughly studied earlier: 1,1′-divinyl-2,2′-biimidazolyl (**8**), 1,2-dimethyl-5-vinyl-imidazo[1,2-*a*]benzimidazole (**9**), and 2-(2-pyridyl)-1-vinylbenzimidazole (**10**). The parameters of ^{1}H NMR spectra of compounds **5**—**10** are presented in Table 1.

For compound **5**, far coupling constants of a proton in the vinyl group, H_X, with those in the imidazole ring, H(4) and H(5), are observed (see Table 1). This interaction (over five and four bonds) is typical of all 2-substi-

Table 1. ^{1}H NMR spectral parameters of compounds **5**—**10**

Compound	δ							*J*/Hz				
	H_A	H_B	H_X	$H_{A'}$	$H_{B'}$	$H_{X'}$	H_{az}	$^2J_{AB}$	$^2J_{A'B'}$	$^5J_{H(4)H_X}$	$^5J_{H(5)H_X}$	$^5J_{H(5)H_{az}}$
5	5.07	5.39	8.13	—	—	—	9.48	−1.8	—	0.55	0.55	0.6
6	5.09	5.39	8.16	5.17	5.63	7.41	9.42	−1.8	−1.2	0.55	0.55	0.6
7	5.45	5.67	7.87	6.21	5.64	7.49	9.62	−0.8	−1.2	—	—	—
8	4.92	5.25	8.06	—	—	—	—	−1.4	—	0.55	0.55	—
9	5.00	6.00	7.07	—	—	—	—	−0.8	—	—	—	—
10	5.28	5.56	7.96	—	—	—	—	−0.8	—	—	—	—

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 10, pp. 1857—1859, October, 1997.

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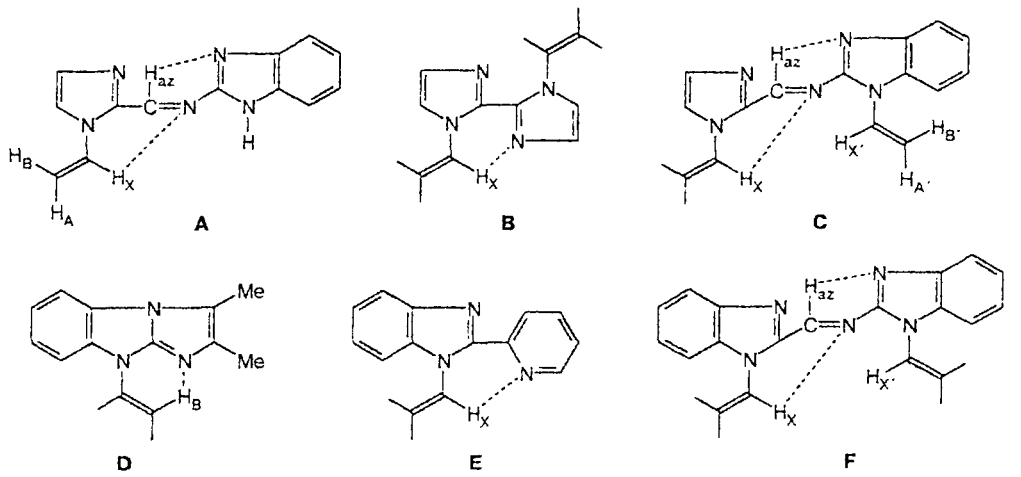

tuted 1-vinylimidazoles.[5–7] The interaction ^1H_X—$^1H(4)$ is transferred through a planar zigzag fragment. Hence, the vinyl group has a preferential *s-trans* orientation with respect to the azomethine group (structure **A**).

In addition, one more far coupling constant, ^5J for the H(5) proton with the proton in the azomethine moiety H_{az}, is observed for compound **5** (see Table 1). Previously,[8] we have observed similar interaction for *N*-(2-thenylidene)- and *N*-(2-furfurylidene)-4-vinyloxyanilines. This interaction was also transferred over a zigzag fragment and indicated a *cis,trans*-orientation of the azomethine and vinyl groups (*E*-isomer, see structure **A**).

The strong downfield chemical shift of the H_X proton signal in the ^1H NMR spectrum of compound **5** (δ 8.13, see Table 1), as opposed to the usual chemical shift for 2-substituted 1-vinylimidazoles observed at δ 6.6—7.0,[5–7] also deserves attention. Two more compounds are also exceptions: **8** (δ 8.06) and **1** (δ 7.92). In the first case, the downfield shift of the signal for H_X is caused by a specific intramolecular interaction (SII) C—H...N resembling weak hydrogen bonds[6,7] (see structure **B**), while in the second case, by the SII C—H...O.[7] In a molecule of compound **5**, conditions for the SII C—H...N involving the N atom of the azomethine group (see structure **A**) are realized to a maximum extent. That is why the strongest downfield shift of the H_X signal occurs.

Another anomaly of the ^1H NMR spectrum is the extremely low-field position for the signal of the azomethine proton, H_{az} (δ 9.48). The maximum chemical shift value ever reported before for H_{az} in vinyloxyphenoxyazomethines is 8.4 ppm.[8] The spatial structure of molecule **5** allows the existence of a second SII, *i.e.*, that between H_{az} and the endocyclic N atom in the benzimidazole ring (see structure **A**), which explains such a large chemical shift for the azomethine H atom.

The spectroscopic parameters of one of the vinyl groups in the divinyl derivative, azomethine **6**, coincides almost completely with those of a monovinyl azomethine **5**. This allows one to assign these signals to the vinyl group bonded to the imidazole ring in the molecule **6**. The three remaining signals correspond to the vinyl group at the benzimidazole ring. Thus, the spatial orientation of one vinyl group in molecules **5** and **6** is the same (see structure **C**). In addition, the chemical shift of H_{az} is not changed considerably as well. Two variants of the spatial orientation of the vinyl group at the benzimidazole ring are possible, namely, *cis*- and *trans*- with respect to the azomethine group. In the former case, the SII C—H_B...N takes place, similar to that in the molecule **9** (see structure **D**), and strong downfield shift of the H_B proton should occur (see Table 1 and Ref. 9). In the molecule **6**, the chemical shift for H_B of the vinyl group in the benzimidazole ring is 5.63 ppm, which is the usual value for 2-substituted 1-vinylbenzimidazoles.[9] In the latter case, the chemical shift for the H_X proton of the aforementioned vinyl group of azomethine **6** (δ 7.41) is noticeably shifted downfield in comparison with the "normal" range of changes for the H_X chemical shift for 2-substituted benzimidazoles (δ 6.9—7.1).[9,10] This shift should be considered as a manifestation of the C—H_X...N interaction in the case of *trans,trans*-orientation of the vinyl and azomethine groups (see structure **C**). The relatively small downfield shift of H_X indicates that the group is displaced from the plane of the benzimidazole ring due to the steric effect of the condensed ring.[7]

The spectroscopic parameters of one vinyl group in the molecule **7** are also very close to the similar parameters of the vinyl substituent at the benzimidazole ring of the molecule **6**. Thus, quite unambiguous assignment of signals for the protons of the vinyl groups at the first and second benzimidazole rings is possible. The insignificance of changes in the parameters of ^1H NMR spectra of the vinyl group at the first benzimidazole ring in the molecule **7** in comparison with those for the molecule **6** allows one to consider that the conformation of this group remains unchanged. It should be noted that the signal for the H_X proton of the vinyl group at the second

benzimidazole ring is observed in even lower field (δ 7.87) than that for the proton of the vinyl group at the first benzimidazole ring. This low-field position of the chemical shift of H_X was observed only for compound **10** (δ H_X 7.96). It is caused by the SII C—H_X...N involving the N atom of the pyridine substituent (see structure **E**). A similar interaction takes place in the molecule **7**, which indicates the preferential *trans,trans*-orientation of the vinyl group at the second benzimidazole ring and the azomethine group (see structure **F**).

Experimental

^{1}H NMR spectra were recorded on a Varian VXR-500 spectrometer (499.8 MHz) in $CDCl_3$ using HMDS as the internal standard.

The starting compounds **1**—**4** were synthesized according to the known procedures.[7,11]

2-(1-Vinylimidazol-2-yl)methyleneaminobenzimidazole (5). A solution of compound **3** (1.33 g, 10 mmol) and compound **1** (1.22 g, 10 mmol) in 20 mL of EtOH was stirred for 1 day at ~20 °C. The resulting yellow precipitate of azomethine **5** was filtered off and dried. Yield 1.8 g (75%), m.p. 245—247 °C. Found (%): C, 65.71; H, 4.60; N, 29.13. $C_{13}H_{11}N_5$. Calculated (%): C, 65.82; H, 4.64; N, 29.54.

1-Vinyl-2-(1-vinylimidazol-2-yl)methyleneaminobenzimidazole (6). A mixture of compound **1** (0.4 g, 3.3 mmol) and compound **4** (0.26 g, (1.65 mmol) was ground and heated for 1 h at 100 °C. The yellow melt was dissolved in 3 mL of hot EtOH and precipitated with water to give azomethine **6**. Yield 0.34 g (67%), yellow flaky crystals, m.p. 107—109 °C. Found (%): C, 68.13; H, 5.27; N, 26.95. $C_{15}H_{13}N_5$. Calculated (%): C, 68.44; H, 4.94; N, 26.62.

1-Vinyl-2-(1-vinylbenzimidazol-2-yl)methyleneaminobenzimidazole (7). A mixture of compound **2** (1.33 g, 6.6 mmol) and compound **4** (1.02 g, 6.6 mmol) was ground and heated for 3 h at 100 °C. The brown melt was triturated with EtOH (4 mL). The resulting bright yellow precipitate was filtered off and dried to give 1.4 g (69%) of azomethine **7**, m.p. 171—172 °C. Found (%): C, 72.61; H, 4.97; N, 22.67. $C_{19}H_{15}N_5$. Calculated (%): C, 72.84; H, 4.79; N, 22.36.

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Received October 30, 1996