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ORIGINAL PAPER

1-Vinylpyrrole-2-carbaldehyde oximes: synthesis, isomerization, and spectral properties

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Abstract The reaction of 1-vinylpyrrole-2-carbaldehydes with hydroxylamine hydrochloride in pyridine or ethanol in the presence of $NaHCO_3$ or NaOAc affords previously unknown 1-vinylpyrrole-2-carbaldehyde oximes in 95–99% yields. Isomerization of oximes from (*E*) to (*Z*) in the presence of strong acids and the spectral characteristics of the isomers were studied.

Keywords (*Z*)/(*E*)-isomers · Protonation · Absorption · Fluorescence

Introduction

Oximes and their derivatives have widespread application in organic synthesis to furnish amines, hydroxylamines, nitriles, diaza compounds, various heterocyclic compounds (isoxazoles, isoxazolidines, pyrroles, pyrrolines, benzofurans, imidazoles, pyridines, oxazines, azirines, aziridines, diaziridines, and palladacycles), as well as metal complexes [1–4]. Oximes of pyrrole series show a wide spectrum of biological activity: bactericidal, acaricidal, growth-regulating, receptor, etc. [5]. A number of oximes are extensively applied in agriculture (the fungicide Fludioxonil [6] and insecticide Chlorfenapyr [7]) and in medicine (the nonsteroidal progesterone receptor agonist Tanaproget [8]). They are also used for the preparation of heterocyclic ensembles [5]. A notable example of the application of pyrrolecarbaldehyde oximes as starting materials is the synthesis of pyrrolylcarbonitriles, which are important building blocks in heterocyclic chemistry [5, 9].

1-Vinylpyrrole-2-carbaldehydes [10, 11] prove to be highly reactive building blocks in organic synthesis [12]. Being involved in the investigations of chemical properties of 1-vinylpyrrole-2-carbaldehydes, we have synthesized a series of 1-vinylpyrrole-2-carbaldehyde oximes. The (*E*)/(*Z*) isomerization of oximes has been known for a long time [13–18]. In many cases the (*Z*)- and (*E*)-isomers of the oximes show different reactivity [5, 21, 22]. In this paper, we report the synthesis of 1-vinylpyrrole-2-carbaldehyde oximes and the study of their (*Z*)/(*E*) isomerization as well as spectral characteristics using ^{1}H and ^{13}C NMR, UV–Vis, luminescence- and IR techniques.

Results and discussion

We have obtained 1-vinylpyrrole-2-carbaldehyde oximes from 1-vinylpyrrole-2-carbaldehydes **1a**–**1e** and hydroxylamine hydrochloride by two procedures [5, 19]: in pyridine (65 °C, 1–1.5 h, method A) and in ethanol in the presence of $NaHCO_3$ or NaOAc (20–25 °C, 1.5–3 h, method B). The yields of the oximes **2a**–**2e** are 95–99% (Scheme 1).

Due to considerable solubility of the oxime **2a** in water method B, involving the washing of the crude product with water, is of limited utility in this case.

In the ^{1}H NMR spectra of the oximes **2a**–**2e**, all the proton signals assigned to the pyrrole moiety, vinyl group

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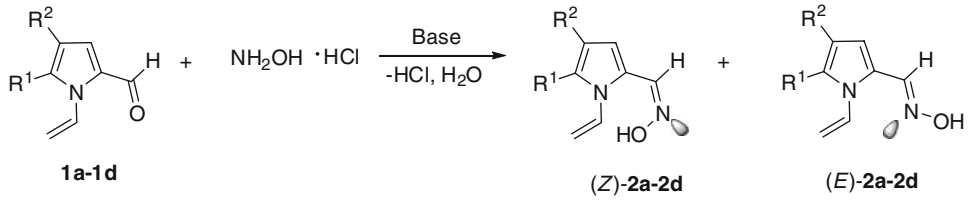
Scheme 1

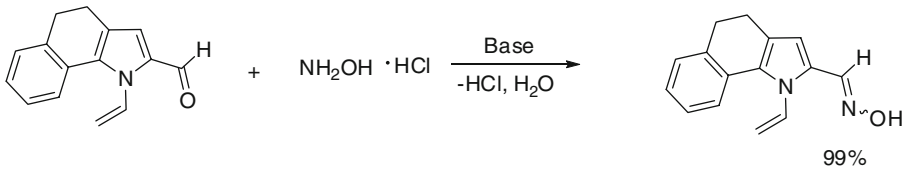


1a-1d (*Z*)-**2a-2d** (*E*)-**2a-2d**

Base = Pyridine, $NaHCO_3$/EtOH, or NaOAc/EtOH

Oxime	R^1	R^2	Yield (%[a])
2a	H	H	95
2b	*n*-Pr	Et	96
2c	Ph	H	99
2d	2-Thienyl	H	97

[a]Isolated



1e 99% (*E*),(*Z*)-**2e**

Base = Pyridine, $NaHCO_3$/EtOH, or NaOAc/EtOH

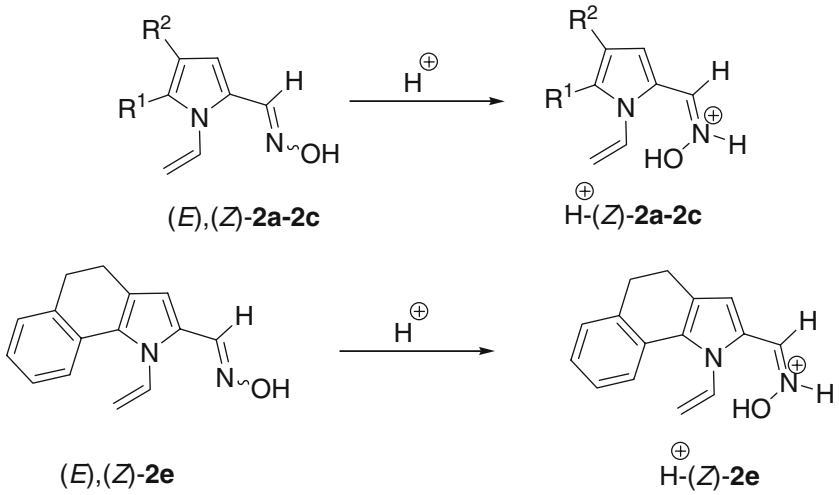
and azomethine fragment are doubled due to (*Z*)/(*E*)-isomerism. All the signals of (*Z*)- and (*E*)-isomers differ significantly (up to 0.8 ppm) from each other. The (*E*)-isomers of oximes **2a–2e** feature low-field resonances of the azomethine protons [13] (8.1–8.2 ppm) as well as lower values of the coupling constants $^1J_{C–H}$ for azomethine protons [20] (164–168 Hz) as compared to the corresponding (*Z*)-isomers (δ = 7.5–7.6 ppm, $^1J_{C–H}$ = 171–179 Hz).

The (*E*)/(*Z*)-isomer ratios of the oximes **2a–2e** depend on the method of preparation. For example, the oxime **2e** prepared by method A contains 42% of (*Z*)- and 58% of (*E*)-isomer, by method B (with $NaHCO_3$) 16% of (*Z*)- and 84% of (*E*)-isomer and by method B (with NaOAc) 36% of (*Z*)- and 64% of (*E*)-isomer. The ratio is not changed on heating up to 70 °C and is practically invariant with the nature of the solvent ($CDCl_3$, C_2D_5OD, C_6D_6, DMSO-d_6) used for recording the ^{1}H and ^{13}C NMR spectra. At a higher temperature (above 90 °C), the ratio of the isomers starts to change. In CCl_4 and hexane, the solubility of the (*Z*)-isomer of **2c** is low, which allows us to isolate this isomer as an individual compound.

It has been found that under the action of strong acids (CF_3SO_3H, CF_3COOH and HCl) (*E*)/(*Z*)-isomerization of 1-vinylpyrrole-2-carbaldehyde oximes **2a–2c**, and **2e** proceeds readily at room temperature. ^{1}H and ^{13}C NMR monitoring of this process ($CDCl_3$) allows some of the regularities (for all compounds and acids used) of (*E*)- and (*Z*)-isomer protonations to be revealed. Successive addition of an acid to the solution of an (*E*)/(*Z*) mixture results in low field shifts of ^{1}H NMR signals for (*Z*)-isomers only, while those for (*E*)-isomers **2a–2c** and **2e** are not shifted at all and eventually disappear with increasing of the acid concentrations. In the ^{1}H NMR spectra, the typical signals of CH=N protons in protonated (*Z*)-isomers H^+-(*Z*)-**2a** to **2c** and H^+-(*Z*)-**2e** are singlets resonated in the region of 8.1–8.2 ppm (see Experimental). These singlets are shifted by ~0.6 ppm towards the low field as compared with that in unprotonated (*Z*)-isomers. The disappearance of (*E*)-isomer signals and increase in integral intensity of protonated (*Z*)-isomers indicate the fact that protonated (*E*)-isomers are transformed rapidly and quantitatively into the corresponding protonated (*Z*)-isomers. The initial ratio of (*E*)- and (*Z*)-isomers as well as the concentration of acid in the solution (up to equimolar ratio oxime:acid) do not affect the process (Scheme 2).

In the ^{1}H NMR spectra, the signals of resinification products of compounds **2b**, **2c** and **2e** are observed when the acids were used in concentrations exceeding equimolar ones.

Scheme 2



In the case of 1-vinylpyrrole-2-carbaldehyde oxime (**2a**), excess HCl leads to the addition of the acid at the vinyl group to furnish a Markovnikov adduct (Scheme 3).

The UV–Vis and fluorescence emission spectra of pure (*Z*)-isomer of **2c** in MeCN are shown in Fig. 1 (absorption $\lambda_{max} = 304$ nm; emission $\lambda_{em} = 365.5$ nm, $\lambda_{ex} = 304$ nm). Unlike the results obtained in DMSO, the equilibrium of (*Z*)/(*E*) isomer **2c** [(*Z*):(*E*) ≈ 1:1] is easily reached under heating of pure (*Z*)-isomer solution in MeCN at 30 °C for 20 h. The UV–Vis and fluorescence emission spectra of (*E*)-isomer could be obtained from the difference spectra of (*Z*)/(*E*) mixture (1:1) and (*Z*) isomer, which are shown in Fig. 1 (absorption $\lambda_{max} = 310$ nm; emission $\lambda_{em} = 375.5$ nm).

In the IR spectrum of the (*Z*)-isomer **2c**, the characteristic absorption bands of oxime ($\bar{\nu}_{C=N} = 1{,}677\ cm^{-1}$, $\bar{\nu}_{N-O} = 955\ cm^{-1}$) and vinyl ($\bar{\nu}_{C=C} = 1{,}636\ cm^{-1}$, $\bar{\nu}_{\tau(HC=CH)} = 913\ cm^{-1}$, $\bar{\nu}_{\omega(=CH_2)} = 850\ cm^{-1}$) functional groups are observed, which have been assigned [22]. Stretching vibrations of the OH moieties of the solid sample appear as a wide band (intermolecular H-bonds, $3{,}165\ cm^{-1}$), while in diluted solutions ($<10^{-3}$ mol dm^{-3}) of CCl_4 the formation of monomer with an intensive narrow peak at $3{,}594\ cm^{-1}$ is observed.

In conclusion, the first representatives of 1-vinylpyrrole-2-carbaldehyde oximes, promising pyrrole synthons and building blocks containing simultaneously vinyl and aldoxime functional moieties, have been obtained and characterized.

Experimental

IR spectra were recorded on a FT-IR spectrophotometer (Excalibur HE 3100). ^{1}H and ^{13}C NMR spectra were run on Bruker DPX-400 and AV-400 instruments; HMDS was used as internal standard. Spectrophotometric measurements were performed on a Lambda 35 Perkin-Elmer spectrophotometer. Fluorescence spectra were recorded on a LS 55 Perkin-Elmer spectrofluorimeter. Elemental analyses (C, H, N, S) were conducted on a ThermoFinnigan 1112 elemental analyzer, and results agreed favorably with the calculated values.

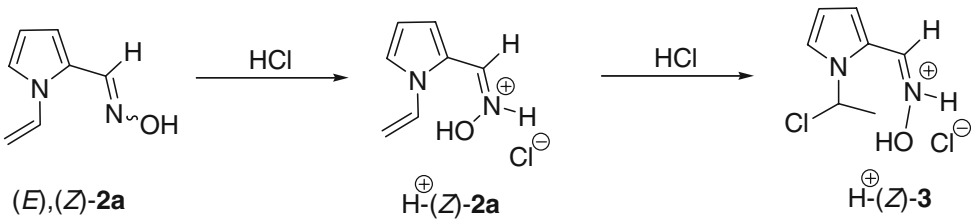
1-Vinylpyrrole-2-carbaldehydes **1a–1e** were synthesized by a modified Vilsmeier–Haack reaction [10, 11]. The reagents were of commercial grade. The solvents were purified by known procedures [23].

General procedures for synthesis of 1-vinylpyrrole-2-carbaldehyde oximes.

Method A

A mixture of 0.25 g 1-vinylpyrrole-2-carbaldehyde (**1a**, 1.1 mmol) and 0.16 g hydroxylamine hydrochloride

Scheme 3



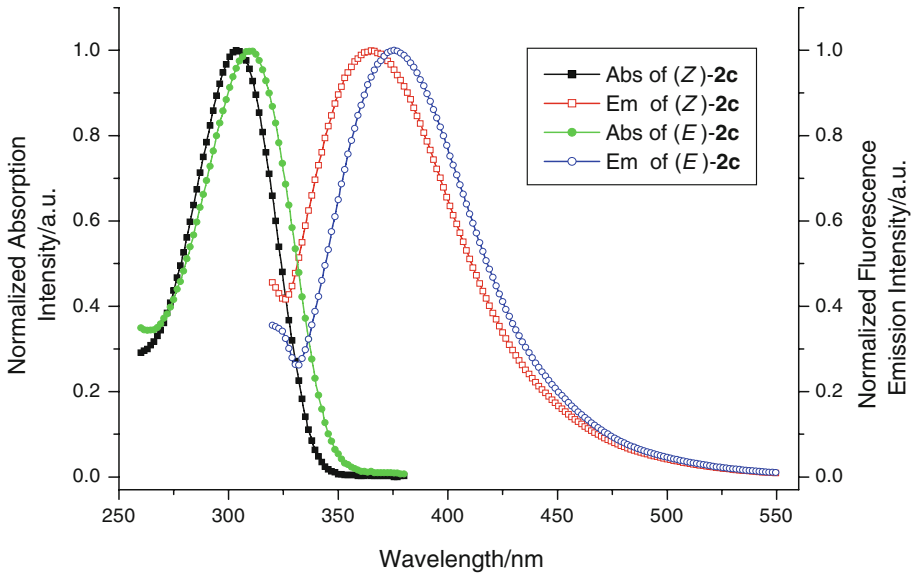


Fig. 1 Normalized UV–Vis absorption and fluorescence emission spectra of (*Z*)- and (*E*)-isomers of **2c** in MeCN (2×10^{-5} mol dm^{-3})

(2.2 mmol) in 2.5 cm^3 pyridine was heated at 65 °C for 1.5 h, and then cooled to room temperature. The mixture was diluted with 2.5 cm^3 water, extracted with diethyl ether (4×10 cm^3) and dried over K_2CO_3. After the ether removal, the mixture was distilled in vacuum (3 mmHg, 50 °C, 3 h) from pyridine traces to afford 0.27 g (95%) of the oxime **2a**.

Method B

A mixture of 0.41 g 5-phenyl-1-vinylpyrrole-2-carbaldehyde **1c** (1.1 mmol), 0.16 g hydroxylamine hydrochloride (2.2 mmol) and 0.12 g $NaHCO_3$ (1.1 mmol) in 2.5 cm^3 ethanol was stirred at room temperature for 2.5 h. Then the mixture was diluted with 10 cm^3 water, the residue was filtered on a Schott filter, washed with 5 cm^3 distilled water and dried on air to give 0.44 g (99%) of the oxime **2c**.

In the ^{1}H NMR spectra of the compounds **2a–2e**, the signals of the hydroxyl proton appear as a broad singlet at 8–9 ppm.

1-Vinylpyrrole-2-carbaldehyde oxime (**2a,** $C_7H_8N_2O$)

Yield 95%, yellowish powder, 50% of (*Z*)-isomer; m.p.: 65–90 °C; ^{1}H NMR (400.13 MHz, $CDCl_3$), (*E*)- ((*Z*)-): $\delta = 8.10$ (7.49) (s, 1H, CHN, $^1J_{C-H} = 164.2$ Hz (172.7 Hz)), 7.55 (6.80) (dd, 1H, H_X, $^3J_{B-X} = 15.7$ Hz, $^3J_{A-X} = 8.6$ Hz), 7.15 (7.08) (d, 1H, H-5, $^3J_{4-5} = 2.8$ Hz), 6.49 (7.41) (d, 1H, H-3, $^3J_{3-4} = 3.7$ Hz), 6.27 (6.37) (dd, 1H, H-4, $^3J_{3-4} = 3.7$ Hz, $^3J_{3-5} = 1.7$ Hz), 5.20 (5.29) (d, 1H, H_B, $^3J_{A-B} = 15.7$ Hz), 4.81 (4.98) (d, 1H, H_A, $^3J_{A-X} = 8.9$ Hz) ppm; ^{13}C NMR (100.61 MHz, $CDCl_3$), (*E*)- ((*Z*)-): $\delta = 142.96$ (135.36) (C=N), 132.65 (130.20) (C_α), 124.80 (122.45) (C-2), 121.70 (121.18) (C-5), 115.77 (119.63) (C-3), 110.74 (111.12) (C-4), 100.56 (104.04) (C_β) ppm.

Protonated (Z)-1-vinylpyrrole-2-carbaldehyde oxime (*H^+-(Z)-**2a***)

^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 8.21$ (s, 1H, CHN), 7.73 (dd, 1H, H-3, $^3J_{3-4} = 3.9$ Hz, $^4J_{3-5} = 1.0$ Hz), 7.38 (dd, 1H, H-5, $^3J_{4-5} = 2.5$ Hz, $^4J_{3-5} = 1.0$ Hz), 7.20 (dd, 1H, H_X, $^3J_{B-X} = 15.1$ Hz, $^3J_{A-X} = 8.3$ Hz), 6.50 (dd, 1H, H-4, $^3J_{3-4} = 3.9$ Hz, $^3J_{4-5} = 2.7$ Hz), 5.40 (dd, 1H, H_B, $^3J_{X-B} = 15.1$ Hz, $^2J_{A-B} = 1.2$ Hz), 5.21 (dd, 1H, H_A, $^3J_{A-X} = 8.3$ Hz, $^2J_{A-B}$ 1.2 Hz) ppm; ^{13}C NMR (100.61 MHz, $CDCl_3$): $\delta = 136.95$ (C=N), 131.3 (C_α), 128.6 (C-5), 128.4 (C-3), 120.1 (C-2), 113.7 (C-4), 105.2 (C_β) ppm.

Protonated (Z)-1-(1-chloroethyl)pyrrole-2-carbaldehyde oxime ***(3)***

^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 8.53$ (s, 1H, CHN), 7.76 (dd, 1H, H-3, $^3J_{3-4} = 3.8$ Hz, $^4J_{3-5} = 1.1$ Hz), 7.48 (dd, 1H, H-5, $^3J_{4-5} = 2.6$ Hz, $^4J_{3-5} = 1.1$ Hz), 6.72 (q, 1H, CHCl, $^3J = 6.1$ Hz), 6.52 (dd, 1H, H-4, $^3J_{3-4} = 3.8$ Hz, $^3J_{4-5} = 2.6$ Hz), 2.14 (d, 3H, CH_3, $^3J = 6.1$ Hz) ppm; ^{13}C NMR (100.61 MHz, $CDCl_3$): $\delta = 134.5$ (C=N), 129.5 (C-5), 128.6 (C-3), 119.8 (C-2), 114.3 (C-4), 64.9 (CHCl), 25.3 (CH_3) ppm.

4-Ethyl-5-propyl-1-vinylpyrrole-2-carbaldehyde (**1b**, $C_{12}H_{17}NO$)

Yield 28%, yellow–orange oily liquid; $n_D^{20} = 1.5754$; ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 9.44$ (s, 1H, CHO), 7.20 (dd, 1H, H_X, $^3J_{B-X} = 15.8$ Hz, $^3J_{A-X} = 8.6$ Hz), 6.85 (s, 1H, H-3), 5.27 (d, 1H, H_A, $^3J_{A-X} = 8.6$ Hz), 5.22 (d, 1H, H_B, $^3J_{B-X} = 15.9$ Hz), 2.61 (m, 2H, $CH_2CH_2CH_3$), 2.43 (q, 2H, CH_2CH_3, $^3J = 7.5$ Hz), 1.55 (m, 2H, $CH_2CH_2CH_3$), 1.18 (t, 3H, CH_2CH_3, $^3J = 7.5$ Hz), 0.94 (t, 3H, $CH_2CH_2CH_3$,

$^3J = 7.3$ Hz) ppm; ^{13}C NMR (100.61 MHz, $CDCl_3$): $\delta = 178.17$ (C=O), 140.32 (C-5), 131.63 (C_α), 131.20 (C-2), 126.37 (C-4), 123.28 (C-3), 111.29 (C_β), 26.54 ($CH_2CH_2CH_3$), 22.54 ($CH_2CH_2CH_3$), 18.88 (CH_2CH_3), 14.93 (CH_2CH_3), 14.03 ($CH_2CH_2CH_3$) ppm; IR (film): $\bar{\nu} = 3{,}111$, 3,046, 2,946, 2,930, 2,871, 2,861, 2,810, 2,723, 1,671, 1,639, 1,580, 1,530, 1,473, 1,420, 1,380, 1,322, 1,282, 1,241, 1,212, 1,157, 1,126, 1,076, 1,029, 960, 915, 881, 854, 802, 773, 746, 710, 682, 593, 514, 481 cm^{-1}.

4-Ethyl-5-propyl-1-vinylpyrrole-2-carbaldehyde oxime (**2b**, $C_{12}H_{18}N_2O$)

Yield 96%, yellow powder, 58% of (*Z*)-isomer; m.p.: 94–149 °C (dec.); ^{1}H NMR (400.13 MHz, $CDCl_3$), (*E*)- ((*Z*)-): $\delta = 8.11$ (7.49) (s, 1H, CHN, $^1J_{C-H} = 163.8$ Hz (171.6 Hz)), 6.91 (6.81) (dd, 1H, H_X, $^3J_{B-X} = 15.9$ Hz, $^3J_{A-X} = 8.6$ Hz), 6.51 (7.31) (d, 1H, H-3, $^3J_{3-4} = 3.9$ Hz), 5.22 (5.36) (d, 1H, H_A, $^3J_{A-X} = 8.6$ Hz), 5.14 (5.23) (d, 1H, H_B, $^3J_{B-X} = 15.9$ Hz), 2.58 (m, 2H, $CH_2CH_2CH_3$), 2.46 (q, 2H, CH_2CH_3, $^3J = 7.5$ Hz), 1.52 (m, 2H, $CH_2CH_2CH_3$), 1.18 (t, 3H, CH_2CH_3, $^3J = 7.5$ Hz), 0.94 (t, 3H, $CH_2CH_2CH_3$, $^3J = 7.3$ Hz) ppm; ^{13}C NMR (100.61 MHz, $CDCl_3$), (*E*)- ((*Z*)-): $\delta = 142.87$ (137.11) (C=N), 133.28 (132.69) (C-5), 131.45 (130.60) (C_α), 124.48 (124.56) (C-4), 123.34 (121.15) (C-2), 111.05 (113.89) (C_β), 26.60 (26.64) ($CH_2CH_2CH_3$), 23.05 (22.83) ($CH_2CH_2CH_3$), 19.00 (19.06) (CH_2CH_3), 15.39 (15.44) (CH_2CH_3), 13.95 (13.95) ($CH_2CH_2CH_3$) ppm.

*Protonated (Z)-4-ethyl-5-propyl-1-vinylpyrrole-2-carbaldehyde oxime (H^+-(Z)-**2b**)*

^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 7.93$ (s, 1H, CHN), 7.64 (s, 1H, H-3), 6.82 (dd, 1H, H_X, $^3J_{B-X} = 15.4$ Hz, $^3J_{A-X} = 8.1$ Hz), 5.70 (dd, 1H, H_A, $^3J_{A-X} = 8.1$ Hz, $^2J_{A-B} = 1.0$ Hz), 5.38 (dd, 1H, H_B, $^3J_{B-X} = 15.4$ Hz, $^2J_{A-B} = 1.0$ Hz), 2.64 (m, 2H, $CH_2CH_2CH_3$), 2.48 (q, 2H, CH_2CH_3, $^3J = 7.3$ Hz), 1.56 (m, 2H, $CH_2CH_2CH_3$), 1.22 (t, 3H, CH_2CH_3, $^3J = 7.3$ Hz), 0.96 (t, 3H, $CH_2CH_2CH_3$, $^3J = 7.1$ Hz) ppm; ^{13}C NMR (100.61 MHz, $CDCl_3$): $\delta = 145.50$ (C-5), 136.19 (C=N), 129.97 (C-4), 128.71 (C_α), 126.58 (C-3), 120.09 (C_β), 118.55 (C-2), 27.17 ($CH_2CH_2CH_3$), 21.94 ($CH_2CH_2CH_3$), 18.87 (CH_2CH_3), 14.44 (CH_2CH_3), 13.94 ($CH_2CH_2CH_3$) ppm.

5-Phenyl-1-vinylpyrrole-2-carbaldehyde oxime (**2c**, $C_{13}H_{12}N_2O$)

Yield 99%, orange powder, 66% of (*Z*)-isomer; m.p.: 85–128 °C (dec.); ^{1}H NMR (400.13 MHz, $CDCl_3$), (*E*)- ((*Z*)-): $\delta = 8.21$ (7.62) (s, 1H, CHN, $^1J_{C-H} = 164.8$ Hz (175.0 Hz)), 7.42–7.26 (7.44–7.29) (m, 5H, Ph), 6.98 (6.80) (dd, 1H, H_X, $^3J_{B-X} = 15.7$ Hz, $^3J_{A-X} = 8.3$ Hz), 6.66 (7.46) (d, 1H, H-3, $^3J_{3-4} = 3.9$ Hz), 6.29 (6.39) (d, 1H, H-4, $^3J_{3-4} = 3.9$ Hz), 4.97 (5.21) (d, 1H, H_A, $^3J_{A-X} = 8.3$ Hz), 5.13 (5.34) (d, 1H, H_B, $^3J_{B-X} = 15.7$ Hz) ppm; ^{13}C NMR (100.61 MHz, $CDCl_3$), (*E*)- ((*Z*)-): $\delta = 143.31$ (137.45) (C=N), 126.26 (123.63) (C-2), 132.55 (132.34) (C_i), 137.45 (136.51) (C-5), 127.52 (127.74) (C_p), 129.09 (129.18) (C_m), 128.42 (128.47) (C_o), 113.18 (119.35) (C-3), 111.38 (111.22) (C-4), 131.85 (131.47) (C_α), 112.05 (114.18) (C_β) ppm.

*Protonated (Z)-5-phenyl-1-vinylpyrrole-2-carbaldehyde oxime (H^+-(Z)-**2c**)*

^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 8.27$ (s, 1H, CHN), 7.93 (d, 1H, H-3, $^3J_{3-4} = 4.4$ Hz), 7.42–7.26 (m, 5H, Ph), 6.81 (dd, 1H, H_X, $^3J_{B-X} = 15.7$ Hz, $^3J_{A-X} = 8.1$ Hz), 6.67 (d, 1H, H-4, $^3J_{3-4} = 4.4$ Hz), 5.67 (dd, 1H, H_A, $^3J_{A-X} = 8.1$ Hz, $^2J_{A-B} = 1.2$ Hz), 5.44 (dd, 1H, H_B, $^3J_{B-X} = 15.7$ Hz, $^2J_{A-B} = 1.2$ Hz) ppm; ^{13}C NMR (100.61 MHz, $CDCl_3$): $\delta = 143.45$ (C-5), 135.51 (C=N), 130.35 (C_i), 129.85 (C_α), 129.12 (C_p), 128.93 (C_m), 128.52 (C_o), 126.18 (C-3), 121.46 (C-2), 117.94 (C_β), 113.81 (C-4) ppm.

*(Z)-5-Phenyl-1-vinylpyrrole-2-carbaldehyde oxime ((Z)-**2c**)*

Hexane (15 cm^3) was added to a solution of 0.50 g 5-phenyl-1-vinylpyrrole-2-carbaldehyde oxime (**2c**, 66% (*Z*)-isomer) in 2 cm^3 diethyl ether under stirring at room temperature; the residue was filtered on a Schott filter, washed with 5 cm^3 hexane and dried on air to give 0.25 g of oxime (*Z*)-**2c** as orange powder (100% of (*Z*)-isomer). m.p.: 135–137 °C (dec.); IR (KBr): $\bar{\nu} = 3{,}165$, 3,056, 3,027, 2,978, 2,923, 2,864, 2,784, 1,677, 1,636, 1,607, 1,453, 1,407, 1,321, 1,283, 1,233, 1,170, 955, 913, 849, 758, 696, 655, 596 cm^{-1}.

5-(2-Thienyl)-1-vinylpyrrole-2-carbaldehyde oxime (**2d**, $C_{11}H_{10}N_2OS$)

Yield 97%, orange powder, 84% (*Z*)-isomer; m.p.: 148–180 °C (dec.); ^{1}H NMR (400.13 MHz, $CDCl_3$), (*E*)- ((*Z*)-): $\delta = 8.16$ (7.55) (s, 1H, CHN, $^1J_{C-H} = 167.4$ Hz (178.5 Hz)), 6.67 (7.47) (d, 1H, H-3, $^3J_{3-4} = 3.9$ Hz), 7.28 (7.28) (dd, 1H, H-3′, $^3J_{3'-4'} = 5.1$ Hz, $^3J_{3'-5'} = 1.0$ Hz), 7.12 (7.12) (dd, 1 H, H-5′, $^3J_{4'-5'} = 3.4$ Hz, $^3J_{3'-5'} = 1.0$ Hz), 7.04 (7.04) (dd, 1H, H-4′, $^3J_{3'-4'} = 5.1$ Hz, $^3J_{4'-5'} = 3.4$ Hz), 6.98 (6.91) (dd, 1H, H_X, $^3J_{B-X} = 15.7$ Hz, $^3J_{A-X} = 8.6$ Hz), 6.38 (6.51) (d, 1H, H-4, $^3J_{3-4} = 3.9$ Hz), 5.29 (5.47) (d, 1H, H_A, $^3J_{A-X} = 8.6$ Hz), 5.18 (5.35) (d, 1H, H_B, $^3J_{B-X} = 15.7$ Hz) ppm; ^{13}C NMR (100.61 MHz, $CDCl_3$), (*E*)- ((*Z*)-): $\delta = 142.71$ (137.00) (C=N), 133.85 (133.85) (C-2′), 131.42 (131.28) (C_α), 130.06 (129.55) (C-5), 127.40 (127.49) (C-4′), 126.68 (124.08) (C-2), 126.67 (126.43) (C-5′), 125.52 (125.68) (C-

3′), 113.69 (115.85) (C_β), 112.29 (119.17) (C-3), 111.84 (111.32) (C-4) ppm.

4,5-Dihydro-1-vinyl-1H-benz[g]indole-2-carbaldehyde oxime (**2e**, $C_{15}H_{14}N_2O$)

Yield 99%, yellow–orange powder, 42% of (*Z*)-isomer; m.p.: 131–174 °C (dec.); ^{1}H NMR (400.13 MHz, $CDCl_3$), (*E*)- ((*Z*)-): $\delta = 8.17$ (7.50) (s, 1H, CHN, $^1J_{C-H} = 164.7$ Hz (173.7 Hz)), 7.20 (7.10) (dd, 1H, H_X, $^3J_{B-X} = 15.7$ Hz, $^3J_{A-X} = 8.0$ Hz), 7.55 (7.57) (m, 1H, H-9), 7.20–7.10 (m, 3H, H-6, H-7, H-8), 6.58 (7.36) (s, 1H, H-3), 5.42 (5.60) (d, 1H, H_A, $^3J_{A-X} = 8.0$ Hz), 5.33 (5.45) (d, 1H, H_B, $^3J_{B-X} = 15.7$ Hz), 2.60 (2.61) (m, 2H, H-4), 2.90 (2.92) (m, 2H, H-5) ppm; ^{13}C NMR (100.61 MHz, $CDCl_3$), (*E*)- ((*Z*)-): $\delta = 142.7$ (137.5) (C=N), 136.9 (136.3) (C-5a), 130.6 (131.4) (C-9b), 126.4 (123.5) (C-2), 132.6 (132.4) (C_α), 128.5 (128.6) (C-7), 128.9 (128.8) (C-9a), 126.3 (126.4) (C-6), 125.8 (126.2) (C-8), 124.6 (124.0) (C-3a), 122.3 (122.5) (C-9), 110.6 (117.2) (C-3), 113.8 (115.6) (C_β), 30.6 (29.7) (C-5), 22.2 (22.2) (C-4) ppm.

*Protonated (Z)-4,5-dihydro-1-vinyl-1H-benz[g]indole-2-carbaldehyde oxime (H^+-(Z)-**2e**)*

^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 8.15$ (s, 1H, CHN), 7.79 (m, 1H, H-9), 7.76 (s, 1H, H-3), 7.38–7.30 (m, 3H, H-6, H-7, H-8), 7.06 (dd, 1H, H_X, $^3J_{B-X} = 15.4$ Hz, $^3J_{A-X} = 8.1$ Hz), 5.90 (dd, 1H, H_A, $^3J_{A-X} = 8.1$ Hz, $^2J_{A-B} = 1.0$ Hz), 5.63 (dd, 1H, H_B, $^3J_{B-X} = 15.4$ Hz, $^2J_{A-B} = 1.0$ Hz), 3.10 (m, 2H, H-5), 2.95 (m, 2H, H-4) ppm; ^{13}C NMR (100.61 MHz, $CDCl_3$): $\delta = 140.9$ (C-9b), 140.7 (C-5a), 139.6 (C-9a), 136.5 (C=N), 130.6 (C_α), 129.4 (C-7), 127.6 (C-3a), 126.3 (C-6), 125.8 (C-8), 125.1 (C-3), 124.9 (C-9), 120.5 (C-2), 120.3 (C_β), 30.4 (C-5), 21.6 (C-4) ppm.

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