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Predominance of (*E*)-1,2-Di(pyridin-2-yl)ethene-1,2-diol over 2-Hydroxy-1,2-di(pyridin-2-yl)ethanone in Solution*

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^{1}H, ^{13}C and ^{15}N NMR spectra, supported by the GIAO/DFT calculated (B3LYP/6-311G//RHF/3-21G) ^{13}C and ^{15}N (B3LYP/6-31++G**//RHF/3-21G) NMR chemical shifts, show that (*E*)-1,2-di(pyridin-2-yl)ethene-1,2-diol (**OO3**) is the only tautomer present in chloroform solution. MP2/6-31G**//RHF/6-31G** and MP2/6-31G** *ab initio* calculations confirm that this perfectly planar form is really more stable than 2-hydroxy-1,2-di(pyridin-2-yl)ethanone (**OK1**, **OK2** and **OK3**) and other isomeric dimers of pyridine-2-carboxaldehyde. The strong intramolecular hydrogen bonds are responsible for high stability of (*E*)-1,2-di(pyridin-2-yl)ethene-1,2-diol (the conjugation in the molecule is of minor importance).

Key words: enols, tautomerism, *ab initio* calculations, NMR spectroscopy, structure elucidation

1,2-Diaryl-2-hydroxyethanones are the products of dimerization of aromatic aldehydes [1]. Although benzoins are usually stable, these obtained from pyridine- and quinoline-2-carboxaldehydes are spontaneously transformed into 1,2-di(pyridin-2-yl)- and 1,2-di(quinolin-2-yl)ethane-1,2-diols, respectively [2–6].

Both simple enols [7,8] and 1,2-enediols, HO–CR=CR–OH, [13] are mostly [9] labile compounds. In general, stability of enediols [8] increases if there are bulky aromatic groups present in the molecule or if there is a carbonyl group conjugated with the enolic C=C–OH moiety [9]. It is noteworthy that there are two strong intramolecular hydrogen bonds in (*E*)-1,2-di(pyridin-2-yl)ethene-1,2-diol. Moreover, its molecule includes an extended π-electron system. On the other hand, there is only one intramolecular hydrogen bond in 2-hydroxy-1,2-di(pyridin-2-yl)ethanone. The parent benzoin, Ph–CH(OH)–CO–Ph, is known to be stable compound (no even traces of enediol, Ph–C(OH)=C(OH)–Ph, were detected in solution). This shows that the strong intramolecular hydrogen bonds may be responsible for high stability of (*E*)-1,2-di(pyridin-2-yl)ethene-1,2-diol, the conjugation in the molecule being of minor importance. *Ab initio* calculations are expected to support or weaken these conclusions.

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It seemed interesting to us to compare the stability of (*E*)-1,2-di(pyridin-2-yl)ethene-1,2-diol and other isomeric dimers of pyridine-2-carboxaldehyde. These compounds are tautomers and rotamers of (*E*)-1,2-di(pyridin-2-yl)ethene-1,2-diol.

EXPERIMENTAL

α-Pyridoin (99%) was that commercially available (Aldrich). ^{1}H, ^{13}C and ^{15}N NMR experiments were run with a Bruker Avance DRX 500 spectrometer working at 500.13 MHz for proton, 125.77 MHz for carbon-13 and 50.69 MHz for nitrogen-15, respectively, and equipped with a 5 mm diameter inverse detection probehead and z-gradient accessory for 0.1–0.2 M solutions in $CDCl_3$ at 303 K. ^{1}H and ^{13}C NMR chemical shift assignments are based on homonuclear two-dimensional (2 D) double quantum filtered (DQF) COSY [10,11] and (2 D) heteronuclear pulsed field gradient (PFG) selected ^{1}H,^{13}C HMQC and HMBC [12] experiments as described in our previous papers [13,14]. ^{1}H and ^{13}C NMR chemical shifts are referenced to the trace signal of $CHCl_3$ (δ = 7.26 ppm from TMS) in proton experiments and the centre peak of $CDCl_3$ (δ = 77.00 ppm from TMS) in carbon-13 experiments. ^{15}N NMR chemical shifts are measured from PFG ^{1}H,^{15}N HMBC correlation maps as before [13,14]. A 1 mm diameter capillary of CH_3NO_2 inserted coaxially inside the 5 mm diameter NMR-tube was used as an external reference for nitrogen-15 chemical shifts. Detailed NMR acquisition and processing parameters are available from E.K. on request. All calculation were carried out with Gaussian 98 package [15]. The optimization at the MP2/6-31G** level was omitted for tautomers/rotamers, which have the relative energy higher than 30 kJ/mol.

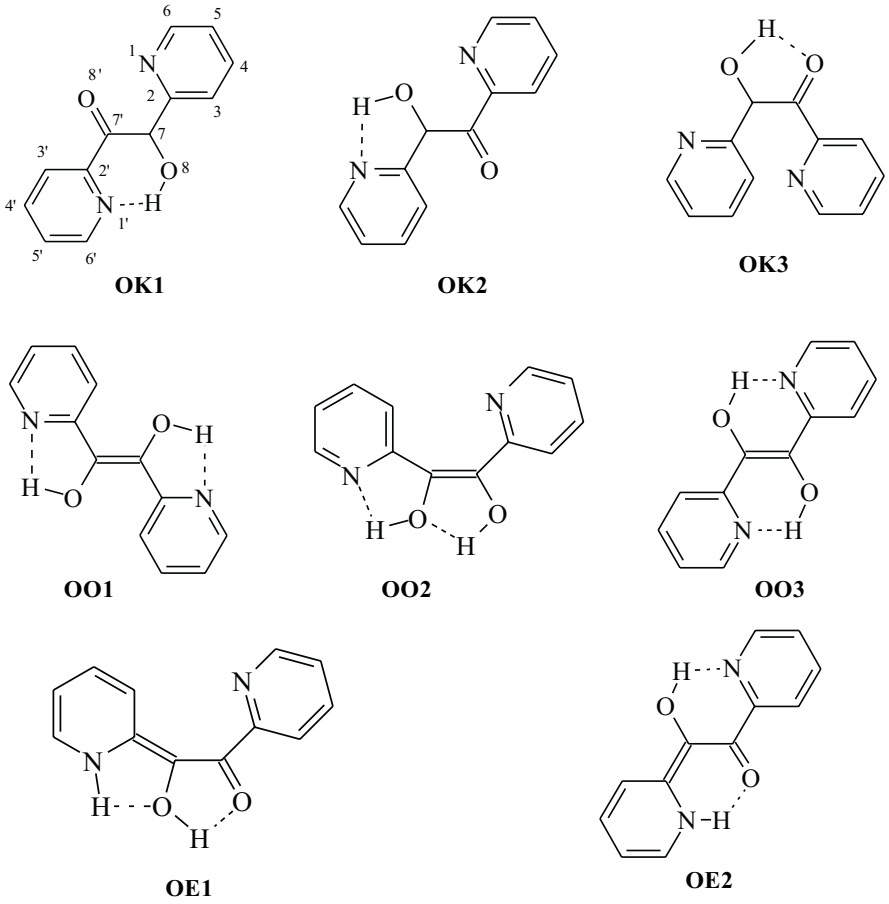
RESULTS AND DISCUSSION

In solution *trans*-1,2-di(pyridin-2-yl)-1,2-ethenediol (α-pyridoin) and *trans*-1,2-di(quinolin-2-yl)-1,2-ethenediol are oxidized by air to respective α-diketones, R–CO–CO–R (R = pyridin-2-yl and quinolin-2-yl) [5,16–19]. The ^{1}H, ^{13}C and ^{15}N NMR signals of the oxidation product (2,2′-pyridyl, dipyridin-2-yl-ethanedione, di-[2]pyridylethanedione) were detected by us for the solution prepared three days before recording the spectra.

Three different conformers of 2-hydroxy-1,2-di(pyridin-2-yl)ethanone are shown in Scheme 1. They are denoted as **OK**. All of them are stabilized by the intramolecular hydrogen bond. On the other hand, three different 1,2-enediols, **OO**, are stabilized by the double hydrogen bonds. Scheme 1 includes also three different hydroxyenaminone tautomers. It is noteworthy that some intramolecular hydrogen bonds in the tautomers/rotamers studied are of O–H...N and some of O–H...O type.

1,2-Enediols being the stable tautomeric forms of benzoins obtained from heterocyclic aldehydes were reviewed [8,20,21]. Enediol structure of the product of benzoin condensation of pyridine-2-carboxaldehyde was confirmed by numerous methods. Thus, signal of the hydroxy protons in the NMR spectrum of *trans*-1,2-di(pyridin-2-yl)-1,2-ethenediol was seen at 12.8 ppm (solution in $CDCl_3$) [22]. This shows that intramolecular interactions taking place in *trans*-1,2-di(pyridin-2-yl)-1,2-ethenediol are responsible for its predomination over α-pyridoin [6,21–24]. This is also the case for its dibenzo derivative [21]. Polarographic studies [25] also show that in

Scheme 1



aqueous alcohol solution (*E*)-1,2-di(2-pyridin-2-yl)ethene-1,2-diol, stabilized by the intramolecular hydrogen bonds, is the only tautomer present.

In crystal the molecule of 1,2-di(pyridin-2-yl)ethene-1,2-diol possesses a centre of symmetry and has a *trans* configuration around the central C–C bond [26]. Within the accuracy of the analysis, the molecule is planar. It contains two intramolecular O–H...N hydrogen bonds. The distances O...N, O–H, and H...N are 259.9, 88 and 178 pm, respectively [26].

Comparison of ^{1}H NMR chemical shifts of the hydroxy proton for α-pyridoin (Table 1) with these for (*Z*)-2-(2-hydroxy-2-phenylvinyl)pyridines (~15.5 ppm) [14] and (*1Z,3Z*)-1,4-di(pyridin-2-yl)buta-1,3-diene-2,3-diol (14.69 ppm) [27] shows that the intramolecular hydrogen bond is weakest in the first compound. ^{13}C chemical shifts of C7 for α-pyridoin (Table 1) and 2-(2-hydroxy-2-phenylvinyl)pyridines (162–165 ppm) [11] are different and the difference between –CH=C(OH)– in 2-(2-hydroxy-2-phenylvinyl)pyridines and –C(OH)=C(OH)– in α-pyridoin is responsible for this behaviour. Moreover, the ^{15}N NMR chemical shift for α-pyridoin (Table 1) is diffe-

rent from these for (*1Z,3Z*)-1,4-di(pyridin-2-yl)buta-1,3-diene-2,3-diol (–112.4 ppm) [27] and 2-(2-hydroxy-2-phenylvinyl)pyridines (–120 to –127 ppm) [14] as well as from that calculated for **OO3** (Table 2). Experimental ^{13}C and ^{15}N NMR chemical shifts (Table 1) can be compared with these calculated for different tautomers/rotamers considered (Table 2). Among them **OO3** shows clearly the best agreement with the experimental ^{13}C chemical shifts (Table 1). It should be mentioned that B3LYP/6-31++G**//RHF/3-21G method used for the calculation of ^{15}N NMR chemical shifts and B3LYP/6-311G//RHF/3-21G used for calculation of ^{13}C NMR chemical shifts were earlier tested for 2-phenacylpyridines and (*Z*)-2-(2-hydroxy-2-phenylvinyl)pyridines [28]. A relatively large difference between the experimental and calculated ^{15}N chemical shifts can be due to the sensitivity of nitrogen-15 shift to the intramolecular interactions and temperature effects, which all are not possible to take into account in theoretical calculations.

Table 1. Experimental ^{1}H, ^{13}C and ^{15}N NMR chemical shifts (δ) of α-pyridoin for 0.4 M solutions in $CDCl_3$ at 303 K and at 223 K (in parentheses).

	δ (ppm)		δ (ppm)
H8(8′)	13.15 (13.72)	C2(2′)	156.53
H6(6′)	8.44 (8.46)	C6(6′)	145.52
H3(3′) and H4(4′)	7.80 (7.89) (7.83–7.88)	C7(7′) C4(4′)	137.37 135.80
H5(5′)	7.14 (7.22)	C3(3′)	121.01
N1(1′)	–103.7	C5(5′)	119.37

Table 2. GIAO/DFT calculated (B3LYP/6-311G//RHF/3-21G) ^{13}C and ^{15}N (B3LYP/6-31++G**//RHF/3-21G) NMR chemical shifts (δ) for different tautomers/rotamers of α-pyridoin.

	OO1	**OO2**	**OO3**	**OE1**	**OE2**	**OK1**	**OK2**	**OK3**
C2	150.77	148.92	157.02	136.14	143.86	158.33	157.98	165.34
C3	127.01	127.51	122.31	127.48	123.06	123.27	122.64	123.24
C4	136.02	135.95	135.97	132.11	133.88	134.42	134.00	135.22
C5	122.08	122.29	121.42	108.35	111.07	123.07	122.78	122.50
C6	145.54	145.23	144.69	130.19	129.88	147.62	148.63	147.09
C7	137.08	137.31	138.02	132.48	131.50	79.50	83.65	72.20
C2′	150.77	152.10	157.02	153.66	159.44	152.29	150.72	152.09
C3′	127.01	124.98	122.31	126.78	124.22	124.51	124.74	122.97
C4′	136.02	135.11	135.97	135.29	135.96	137.22	135.55	135.10
C5′	122.08	121.79	121.42	124.60	123.98	128.38	127.52	127.69
C6′	145.54	145.20	144.69	144.79	144.79	147.23	146.94	148.56
C7′	137.08	141.79	138.02	172.18	165.53	201.69	206.60	209.90
N1	–114.10	–113.01	–119.17	–271.03	–262.59	–78.39	–87.40	–83.12
N1′	–114.10	–95.83	–119.17	–92.37	–110.42	–96.88	–78.99	–71.79

The RHF/6-31G** calculations show that molecules **OO1**, **OO2**, **OO3**, and **OE2** were found to be perfectly planar in vacuum. Some important dihedral angles [deg] and bond lengths [pm] in the tautomers/rotamers studied were: **OK1** (H8O8C7C7′: –70.46, N1C2C7C7′: 81.80, N1′C2′C7′O8′: 176.68, C3C2C7O8: 23.13, O8H8: 94.56), **OK2** (H8O8C7C2: –33.00, N1C2C7O8: 8.51, O8′C7′C7O8: 137.44, N1′C2′C7′O8′: 163.27, O8H8: 94.71), **OK3**: (N1C2C7O8: 98.69, C2C7C7′O8′: 111.09, H8O8C7C7′: 24.15, N1′C2′C7′O8′: 169.92, O8H8: 94.73), **OO1**: (O8H8: 95.06), **OO2**: (O8H8: 95.08), O8′H8′: 94.52), **OO3**: (O8H8: 95.39), **OE1**: (N1H1: 100.51; O8H8: 94.84). The hydrogen bond lengths in the compounds studied, calculated with different methods, are presented in Table 3.

Table 3. Calculated hydrogen bond lengths [pm] in different tautomers/rotamers of α-pyridoin.

	Method	(O)H...N	(O)H...O	(N)H...O
OK1	a	220	–	–
	b	218	–	–
	c	202	–	–
OK2	a	221	–	–
	b	225	–	–
	c	209	–	–
OK3	a	–	210	–
	b	–	214	–
	c	–	201	–
OO1	a	193	–	–
	b	193	–	–
	c	184	–	–
OO2	a	187	190	–
	b	209	206	–
OO3	a	183	–	–
	b	182	–	–
	c	171	–	–
OE1	a	–	198	205
	b	–	202	207
OE2	a	188	–	179
	b	186	–	179

[a]RHF/6-31G**, *in vacuum.* [b]RHF/6-31G**, solution in chloroform (PCM model of solvation).
[c]MP2/6-31G**, *in vacuum.*

Theoretical calculations were found very useful to estimate the energies of different tautomers [27]. The results for the species considered in the present paper are collected in Table 4. **OO3** is the most stable tautomeric form both in vacuum and in chloroform solution. It is stabilized by two intramolecular hydrogen bonds of RAHB

(Resonance-Assisted Hydrogen Bond) type [29] and by the extended π-electron system in its molecule. As expected, the O–H...O hydrogen bond in **OO2** is not as strong as O–H...N in **OO1**. This results in higher stability of **OO1** as compared to that of **OO2**. All three **OK** forms have higher energies than **OO1**. It seems interesting that energetic differences between **OK1**, **OK2** and **OK3** are not high. The **OE** forms have the highest energies among all tautomers studied. On the other hand, of all **OE** tautomers **OE2** was found to be most stable. Since the polarization continuum model (included in Gaussian 98 package) do not consider nature of the interactions between the chloroform nitrogen atom and carbonyl group or aza atom, one should aware of some doubt in the calculated energies of different tautomers in solution. It can be seen, however, that the most stable **OO3** form is the only species detected.

Table 4. Calculated relative energies (kJ mol^{-1}) for α-pyridoin and its tautomers/rotamers.

	MP2/6-31G**//RHF/6-31G** *in vacuum*	MP2/6-31G**//RHF/6-31G** PCM in chloroform	MP2/6-31G** *in vacuum*
OO3	0.00	0.00	0.00
OK3	19.45	20.91	19.98
OK2	23.87	24.04	24.88
OO1	24.20	24.80	26.21
OK1	26.38	23.21	27.73
OE2	47.16	45.80	–
OO2	52.72	52.33	–
OE1	95.92	90.71	–
a	–721.1301558	–721.1324595	–721.1386207

[a]Total energy (au) of the most stable tautomer/rotamer.

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