

Dependence of Carbon Chemical Shifts in the ^{13}C NMR Spectra of 5-Hydroxy-1,4-naphthoquinon-4-imines on Position of Tautomeric Equilibrium

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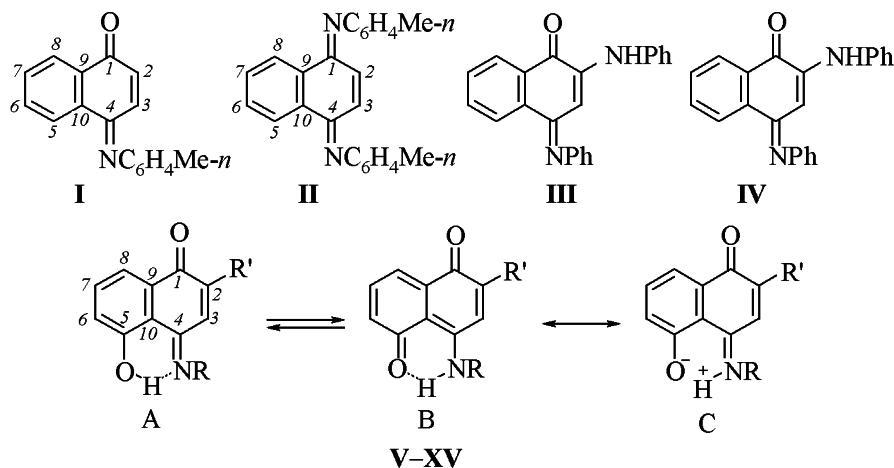
Abstract—In the ^{13}C NMR spectra of 5-hydroxy-1,4-naphthoquinon-4-imines the *para*-quinonimine form is characterized by the presence of signals from C^5 in the region 160–162 ppm and from C^{10} at ~115 ppm whereas typical signals of the *ana*-quinonoid form are those of C^5 in the region 169–170 ppm and C^{10} at 110–111 ppm.

^{13}C NMR spectroscopy is widely used in the studies of tautomeric transformations of organic compounds, among them also of quinoid systems [1–3]. We showed formerly that 5-hydroxy-1,4-naphthoquinon-4-imines dissolved in organic solvents were present as a mixture of *para*- and *ana*-tautomers [4]. The effect of substituents and solvent character on the position of the tautomeric equilibrium was investigated by means of ^1H NMR and electron absorption spectroscopy [4, 5]. No published ^{13}C NMR spectra exist for 1,4-naphthoquinon-4-imines and 4,8-diamino-1,5-naphthoquinones.

In the presents study by comparison with the spectra of model compounds **I–IV** was investigated

the effect of position of tautomeric equilibrium on the chemical shifts in the ^{13}C NMR spectra of 5-hydroxy-1,4-naphthoquinon-4-imine derivatives (**V–XV**) taken in CDCl_3 (see table).

As a model of *para*-quinonimine form **A** was selected *N*-(*p*-tolyl)-1,4-naphthoquinon-4-imine (**I**). The comparison of ^{13}C NMR spectra of 1,4-naphthoquinone [6–8] and *N,N'*-di(*p*-tolyl)-1,4-naphthoquinonediimine (**II**) suggested the assignments of the signals in the spectrum of compound **I**. The chemical shift of carbonyl carbon atom in *para*-quinonimine **I** (185.49 ppm) is close to the value δ_{C} 184.9 ppm observed in 1,4-naphthoquinone [6], the signals of carbon atoms in the $\text{C}=\text{N}$ bond (~155 ppm) are some-



$\text{R} = \text{C}_6\text{H}_4\mu\text{-p}$, $\text{R}' = \text{H}$ (**V**); $\text{R} = \text{Ph}$, $\text{R}' = \text{H}$ (**VI**); $\text{R} = \text{C}_6\text{H}_4\text{NO}_2\text{-p}$, $\text{R}' = \text{H}$ (**VII**); $\text{R} = \text{Bu}$, $\text{R}' = \text{H}$ (**VIII**); $\text{R} = \text{Ph}$, $\text{R}' = \text{SO}_2\text{Ph}$ (**IX**); $\text{R} = \text{Ph}$, $\text{R}' = \text{NHPh}$ (**X**); $\text{R} = \text{Ph}$, $\text{R}' = \text{NHBu}$ (**XI**); $\text{R} = \text{Bu}$, $\text{R}' = \text{NHBu}$ (**XII**); $\text{R} = \text{Bu}$, $\text{R}' = \text{NHPh}$ (**XIII**); $\text{R} = \text{Bu}$, $\text{R}' = 1\text{-piperidino}$ (**XIV**); $\text{R} = \text{Me}$, $\text{R}' = \text{NHMe}$ (**XV**).

Table 6. Chemical shift (δ_C , ppm) of carbon atoms in 1,4-naphthoquinonimines (**I–XV**) and 4,8-dibutylamino- (**XVI**) and 4,8-diphenylamino- (**XVII**)-1,5-naphthoquinonimines

Compd. no	C ¹	C ²	C ³	C ⁴	C ⁵	C ⁶	C ⁷	C ⁸	C ⁹	C ¹⁰	Other carbons
I	185.49	133.80	133.10	154.89	125.36	130.43 ^a	131.22 ^a	125.98	131.69	134.13	20.84, 120.78, 129.78, 135.39, 147.58
II	155.62	130.40	130.40	155.62	124.82	125.39	125.39	124.82	134.15	134.15	20.53, 120.44, 129.40, 133.54, 147.92
III	181.55	151.13	97.46	155.01	125.26 ^a	130.336	133.386	126.24 ^a	130.03	135.66	120.56, 123.81, 123.94, 128.62, 129.27, 132.55, 139.76
IV	181.87	142.72	91.37	154.63	124.49	129.10 ^a	132.88 ^a	125.59	129.66	136.92	13.66, 13.96, 20.18, 20.80, 30.37, 33.49, 41.99, 51.33
V	184.86	135.02	132.75	159.46	160.57	123.48	130.07	118.07	131.40	115.69	20.86, 122.18, 129.68, 136.36, 142.90
VI	184.53	135.16	132.78	159.63	160.49	123.41	129.88	118.05	131.37	115.47	121.93, 126.12, 129.88, 145.43
VII	184.21	136.64	133.94	160.59 ^a	160.81 ^a	124.04	129.60	118.99	131.54	115.08	122.35, 125.00, 145.65, 151.40
VIII	184.92	135.34	132.22	160.31	162.29	124.20	126.94	117.44	131.06	115.25	13.66, 20.41, 32.98, 49.11
IX	178.47	144.23	134.15	157.32	160.59	124.32	132.29	119.10	131.26	115.60	122.50, 127.75, 128.92, 129.31, 129.62, 133.57, 138.70, 145.02
X	181.14	146.20	95.78	160.95 ^a	161.35 ^a	124.49	131.86	118.53	130.21	115.30	121.15, 122.51, 125.12, 125.30, 128.32, 129.39, 138.11, 141.15
XI	183.09	146.23	92.01	161.18 ^a	161.88 ^a	124.93	131.56	118.10	130.41	115.30	13.54, 19.98, 30.26, 41.85, 122.60, 125.23, 128.91, 147.04
XII	180.26	146.58	87.65	161.86	170.63	130.96	131.97	116.32	129.66	110.02	13.54, 20.06, 20.21, 30.10, 31.43, 42.16, 44.53
XIII	180.54	143.12	91.31	161.61	169.03	132.06	137.62	117.14	129.71	111.77	13.60, 20.23, 31.91, 45.46, 122.35, 125.39, 129.95, 137.62
XIV	182.49	153.14	97.99	161.39	169.17	128.58	132.14	116.45	132.49	111.38	13.62, 20.25, 24.08, 25.53, 31.65, 44.95, 50.27
XV	180.24	147.64	87.28	163.18	170.64	131.15	132.10	116.58	129.58	111.50	29.12, 31.45
XVI	176.63	137.82	124.08	150.68	176.63	137.82	124.08	150.68	109.12	109.12	13.53, 20.04, 31.75, 42.60
XVII	175.87	135.63	125.96	149.24	175.87	135.63	125.96	149.24	110.43	110.43	124.64, 126.43, 129.38, 139.80

^{a,b} No exact assignments, the δ_C marked with the same letters are interchangeable.

what shifted upfield as compared to the ^{13}C NMR spectra of *N*-aryl-1,4-benzoquinon-4-imines (δ_{C} 157.14 ppm) [9].

The C=N group as also the carbonyl group due to the combined effect of anisotropy and electron-withdrawing character induce upfield shift of located in *peri*-position C^5 and C^8 , and downfield shift of C^2 and C^3 as compared with the signals from the corresponding atoms in naphthalene spectrum.

An arylamino group introduced into position 2 (compound **III**) causes a large downfield shift of the signal from C^2 and an upfield shift of signals from C^7 and C^3 , as is observed in 2-amino derivatives of 1,4-naphthoquinone [16]. The comparison of spectra belonging to *N*-phenyl-2-phenylamino-1,4-naphthoquinon-4-imine (**III**) and to *N*-butyl-2-butylamino-1,4-naphthoquinon-4-imine (**IV**) showed that for 2-amino-substituted 1,4-naphthoquinon-4-imines the chemical shift of C^4 carbon in the C=N bond is weakly affected by the substituent at the nitrogen atom (δ_{C} ~155 ppm). Besides the substituents in the quinoid part of the molecule virtually do not affect the position of signals from carbon atoms of the aromatic ring (cf. spectra of compounds **I**, **III**, and **IV**).

The comparison of ^{13}C NMR spectra of compounds **I** and **V** showed that a hydroxy group in 5 position as should be expected causes a strong deshielding of the *ipso*-carbon ($\Delta\delta$ +35.21 ppm) and an upfield shift of signals from atoms C^6 , C^8 , and C^{10} . A downfield shift by 4.57 ppm of the signal from C^4 atom is apparently due to formation of an intramolecular hydrogen bond between the proton of the hydroxy group and the nitrogen of the *peri*-located C=N bond. A similar downfield shift by 5.2 ppm of the signal from the carbon atom in the carbonyl group forming an intramolecular hydrogen bond with the *peri*-located OH group is observed at going from 1,4-naphthoquinone to 5-hydroxy-1,4-naphthoquinone [7].

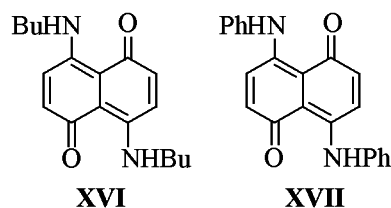
The comparison of spectra of a series of *N*-alkyl-(aryl)-5-hydroxy-1,4-naphthoquinon-4-imines (**V–VIII**) showed that the change in the character of a substituent at the nitrogen atom from alkyl to *para*-nitrophenyl group slightly affected the chemical shifts of carbon atoms in C–H bonds and also of the atoms C^4 and C^5 ; the position of signals from the atoms C^1 , C^9 , and C^{10} remained virtually intact. The introducing of substituents into 2 position of 5-hydroxy-*N*-phenyl-1,4-naphthoquinon-4-imine (compounds **IX–XI**) resulted in significant deshielding of C^2 atom ($\Delta\delta$ 9–11 ppm) and depending on electronic effect provided more or less notable (1–6 ppm) upfield shift

of the signal from the carbonyl carbon C^1 . Therewith the introduction of an electron-withdrawing substituent (SO_2Ph , compound **IX**) caused a slight downfield shift of the signal from C^3 atom, and the electron-donor substituents PhNH and AlkNH in the same position (compounds **X**, **XI**) gave rise to a strong upfield shift of atom C^3 signal ($\Delta\delta$ 37–40 ppm) as was observed for 2-substituted derivatives of 1,4-naphthoquinone [6, 8].

It should be noted that in all the above 5-hydroxy-1,4-naphthoquinon-4-imines (**V–XI**) which according to electron absorption spectra in organic solvents including chloroform are present predominantly in the *para*-quinonimine form A [4, 5, 10] the range of chemical shifts of signals from C^4 and C^5 is narrow (~4 and ~2 ppm respectively). A characteristic feature of their ^{13}C NMR spectra is the presence of signals from C^5 in the region 160–162 ppm and those from C^{10} at 115.08–115.69 ppm; the position of these signals is virtually the same as in the spectra of 5-hydroxy-1,4-naphthoquinones [6, 7].

The strongest variations in the carbon chemical shifts were observed in the spectra of 5-hydroxy-1,4-naphthoquinon-4-imines (**XII–XV**) containing simultaneously an amino group at C^2 and *N*-alkyl group at the quinonimine carbon atom. According to the data of electron absorption and ^1H NMR spectra these compounds in chloroform are predominantly in the *ana*-quinoid form B [4, 5, 11].

As models of *ana*-quinoid form B we chose 4,8-di-butylamino- (**XVI**) and 4,8-diphenylamino-1,5-naphthoquinones (**XVII**) [12, 13] that are characterized by signals of carbonyl carbons at ~176 ppm and of C^9 , C^{10} atoms at 109–110 ppm.



Unlike the spectra of compounds **V–XI** existing in the *para*-quinonimine form A in the ^{13}C NMR spectra of compounds **XII–XV** the signals from C^5 atom are considerably displaced downfield (to 169–170 ppm) and by the absolute value are located between the resonance regions of C–O⁻ bond (168 ppm) [14] and that of a carbonyl group in the 4,8-diamino-*ana*-naphthoquinones (~176 ppm); the signals from C^{10} atoms are notably shifted upfield (to 110–111 ppm)

and are close in the chemical shift values to those of C^9 , C^{10} atoms in the model *ana*-naphthoquinones.

EXPERIMENTAL

^{13}C NMR spectra were registered on spectrometers Bruker DRX-500, AC-200, and AM-400 from solutions in $CDCl_3$ with complete decoupling from protons in the *J*-modulation mode, chemical shifts were measured with respect to the solvent signal (76.9 ppm).

The compounds studied were synthesized by the following procedures: (I) [15], (II) [16], (III) [17], (IV) [18], (V-VII) [10], (VIII), (XII), [11], (IX) [19], (X) [20], (XI), (XIII) [21], (XIV) [4], (XV) [21], (XVI) [12], (XVII) [13].

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