^{13}C NMR SPECTRA OF 8-MERCAPTOQUINOLINE AND 8-HYDROXYQUINOLINE

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The signals in the ^{13}C NMR spectra of quinoline and its 8-substituted derivatives (SH, SCH_3, OH, OCH_3, NH_2, I, and CH_3), 8,8'-diquinolyl disulfide, the 8-hydroxy-N-methylquinolinium ion, and the protonated and anionic forms of 8-hydroxy- and 8-mercaptoquinoline were assigned. The increments of the substituents in the neutral forms of these compounds correlate satisfactorily with those in substituted benzenes and the Swain–Lupton parameters (r = 0.94-0.99). The differences in the ortho increments of the substituents are due to a change in the electron densities on the carbon atoms and also to steric hindrance. The effect of an intramolecular hydrogen bond on the ^{13}C chemical shift of the quinoline ring of 8-hydroxy- and 8-mercaptoquinoline was examined. The ^{13}C chemical shifts correlate satisfactorily with the total charges (q) on the carbon atoms in the neutral forms of these compounds. A similar correlation is satisfied to a lesser extent for the protonated and anionic forms because of a change in the bond orders.

The physicochemical properties of the widely used analytical reagent 8-mercaptoquinoline and its chelate compounds with metal ions were examined in [1]. In a continuation of studies of the electronic structure of this compound and its well-known oxygen-containing analog, 8-hydroxyquinoline, in the present research we examined the ^{13}C NMR spectra of quinoline (I), 8-mercapto- (II), 8-S-methyl- (III), 8-hydroxy- (IV), 8-methoxy- (V), 8-amino- (VI), 8-iodo- (VII), and 8-methylquinoline (VIII), 8,8'-diquinolyl disulfide (IX), 8-hydroxy-N-methylquinolinium ion (X), and the protonated forms of I-V (Io-Vo) and the ionic forms of II and IV (IIa and IVa). Compounds I and VI-VIII are included in this series in order to make a correlation analysis of the ^{13}C chemical shifts, while X is a standard substance in the study of the electronic structure of the mesoionic form of 8-mercaptoquinoline [2].

The signals were assigned on the basis of the spectra without decoupling of the protons (with the Overhauser nuclear effect) or with extraresonance suppression of the spin–spin coupling. The ^{13}C chemical shifts of I-X, Io-Vo, IIa, and IVa and the increments of the substituents are presented in Tables 1 and 2. The charges on the atoms calculated within the CNDO/2 approximation (with the parametrization of the atoms and the geometry of the molecules in [2, 3]) are also presented in Table 1.

The increments of the substituents in the II-VIII molecules correlate satisfactorily with those for substituted benzenes ($\Delta\delta^B$):

$$\Delta\delta_\alpha = 0{,}83\Delta\delta_\alpha{}^B + 1{,}23\ (r = 0{,}99),$$

$$\Delta\delta_p = 1.55\Delta\delta_n{}^B + 1.50\ (r = 0{,}94).$$

A correlation between the $\Delta\delta_p$ values and the Swain-Lupton substituent parameters, which is similar to the correlation for substituted benzenes, follows naturally from the observed correlation between the $\Delta\delta_p$ and the $\Delta\delta_p^B$ values of the substituents:

$$\Delta\delta_p = 3{,}5F + 16{,}9R - 0.8\ (r = 0.94).$$

The $\Delta\delta_p$ and σ^+ constants of the substituents correlate somewhat more poorly:

$$\Delta\delta_p = 10.1\sigma^+ - 1{,}2\ (r = 0.88).$$

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TABLE 1. ^{13}C Chemical Shifts (δ^a, ppm) and Total Charges (q) on the Atoms in I-X, Io-Vo, and IIa-IVa

Atom No.	I		II				III		IV		V	
	q	δ	q	δ	δ^b	δ^c	q	δ	q	δ	q	δ
2	0,099	150,7	0,095	149,7	149,2	149,2	0,094	149,4	0,095	148,5	0,091	149,4
3	−0,026	121,6	−0,022	122,0	121,6	122,1	−0,022	122,2	−0,019	122,1	−0,018	122,1
4	0,034	136,4	0,031	137,2	136,6	138,2	0,030	136,7	0,030	136,7	0,027	136,2
5	−0,001	128,4	−0,024	124,9	126,5	124,8	−0,023	123,9	−0,032	118,5	−0,032	120,1
6	0,002	127,0	0,016	126,9	124,3	127,3	0,015	127,2	0,025	128,4	0,025	127,2
7	0,017	129,9	−0,023	127,4	126,8	128,5	−0,026	123,2	−0,055	111,5	−0,067	108,2
8	−0,022	129,9	0,049	135,4	135,8	136,3	0,042	140,6	0,165	153,3	0,167	155,9
9	0,101	148,8	0,079	144,1	143,7	143,8	0,081	145,8	0,052	138,8	0,058	140,7
10	0,012	128,8	0,022	129,1	129,0	129,4	0,021	128,5	0,029	129,3	0,029	129,7

TABLE 1 (continued)

Atom No.	VI		VII	VIII		IX	X			Io	
	q	δ	δ	q	δ	δ	q	δ	δ^c	q	δ^d
2	0,095	147,8	151,8	0,096	149,0	150,4	0,109	146,2	146,6	0,190	144,9
3	−0,021	121,7	122,4	−0,024	120,6	122,3	−0,037	124,2	123,7	−0,046	122,8
4	0,031	136,4	137,2	0,033	136,0	137,3	0,076	143,0	146,6	0,132	149,4
5	−0,022	116,4	129,3	−0,011	125,8	125,8	−0,096	106,4	110,5	0,035	130,2
6	0,017	127,9	128,2	0,007	126,1	127,4	0,060	133,2	132,3	0,014	131,6
7	−0,031	110,4	140,5	−0,005	129,5	125,2	−0,109	118,9	119,9	0,075	136,9
8	0,095	146,6	104,1	0,020	136,9	136,0	0,176	167,2	164,6	−0,036	120,9
9	0,071	138,8	147,3	0,088	147,3	146,4	0,050	$134,7^d$	$134,0^d$	0,155	137,7
10	0,022	129,4	129,2	0,015	128,1	128,8	0,037	$134,0^d$	$133,5^d$	0,011	130,0

TABLE 1 (continued)

Atom No.	IIo		IIIo		IVo		Vo		IIa			IVa	
	q	δ^e	q	δ^e	q	δ^e	q	δ^e	q^f	q^g	δ^e	q	δ^e
2	0,187	145,3	0,186	145,1	0,186	143,0	0,185	142,8	0,053	0,108	149,0	0,043	146,8
3	−0,043	122,9	0,044	123,0	−0,040	122,6	−0,041	122,5	−0,027	−0,032	121,0	−0,024	121,1
4	0,129	148,2	0,128	149,0	0,127	147,0	0,126	146,7	0,003	0,045	137,8	−0,006	137,0
5	0,011	127,3	0,009	127,1	−0,003	119,2	−0,004	119,4	−0,096	−0,043	121,0	−0,130	111,6
6	0,027	130,2	0,027	130,7	0,041	131,1	0,039	130,7	0,032	0,026	126,8	0,051	129,3
7	0,032	138,3	0,027	134,5	−0,020	116,4	−0,024	112,6	−0,099	−0,040	134,3	−0,162	115,0
8	0,030	126,1	0,024	130,4	0,172	146,4	0,172	147,9	0,110	0,086	151,3	0,182	165,5
9	0,130	136,6	0,129	134,5	0,102	127,1	0,098	128,4	0,054	0,074	150,5	0,021	144,6
10	0,020	129,2	0,020	129,3	0,029	129,2	0,029	127,0	0,021	0,021	130,2	0,033	131,4

[a] Relative to tetramethylsilane. [b] In cyclohexane + $CDCl_3$ (7:1). [c] In CD_3OD. [d] The assignment is invariant. [e] In D_2O. [f] Calculation of model C. [g] Calculation of model D.

Because of the difference in the ortho increments of the substituents (Table 2) the correlation of $\Delta\delta_o^B$ was made with the average values $\Delta\bar{\delta}_o = (\Delta\delta'_o + \Delta\delta''_o)/2$ (where $\Delta\delta'_o$ and $\Delta\delta''_o$ are the shifts of the C_7 and C_9 signals, respectively):

$$\Delta\bar{\delta}_o = 0.89\Delta\delta_o{}^B - 2.37 \ (r = 0.97).$$

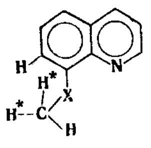
According to these data, the nature of the coupling of the SR and OR groups with the quinoline ring in the 8 position is similar to that in substituted benzenes.

In III-VIII the difference ($\Delta\delta_o$) in the substituents ($|\Delta\delta'_o| > |\Delta\delta''_o|$) is partially due to the large increase of the negative charge on the C_7 atom relative to C_9 in the case of exocyclic substitution in the I molecule [4]. Shielding of C_7 as a consequence of steric hindrance on the part of the SCH_3 and OCH_3 groups (the trans configuration of III and V) is also superimposed on this effect in III and V. According to the calculation ($\delta = 1680\ e^{-2.671}\cos\theta$ [5]), polarization of the C_7—H_7 bond in the III (V) molecules leads to 5 and 14 ppm (7 and 36 ppm) shifts of the C_7 signal to strong field for trans configurations A and B, respectively. The experimental value of the shift of the C_7 signal in III (V) relative to I is −6.7 ppm (−21.7 ppm). It must be noted that, for example in the trans

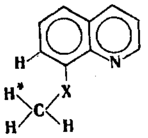
TABLE 2. Increments of the Substituents in II-IX, IIo-Vo, and IIa and IVa

Substituent (compound)	$\Delta\delta_\alpha$	$\Delta\delta'_o$ (C_7)	$\Delta\delta''_o$ (C_9)	$\Delta\delta'_m$ (C_6)	$\Delta\delta''_m$ (C_{10})	$\Delta\delta_p$
SH (II)	5,5	−2,5	−4,7	−0,1	0,3	−3,5
SH (IIo)	5,2	1,4	−1,1	−1,3	−0,8	−2,9
S^- (IIa)	21,4	4,4	1,7	−0,2	1,4	−7,4
SCH_3 (III)	10,7	−6,7	−3,0	0,2	−0,3	−4,5
SCH_3 (IIIo)	9,5	−2,4	−3,2	−0,9	0,5	−3,1
OH (IV)	23,4	−18,4	−10,0	1,4	0,5	−9,9
OH (IVo)	25,5	−20,5	−10,6	−0,5	−0,8	−11,0
O^- (IVa)	35,6	−14,9	−4,2	2,3	2,6	−16,8
OCH_3 (V)	26,0	−21,7	−8,1	0,2	1,0	−8,3
OCH_3 (Vo)	27,0	−24,3	−9,3	−0,9	−3,0	−10,8
NH_2 (VI)	14,7	−19,5	−10,0	0,9	0,6	−12,0
I (VII)	−25,8	10,6	−1,5	1,2	0,4	0,9
CH_3 (VIII)	7,0	−0,4	−1,5	−0,9	−0,7	−2,6
C_9H_6NSS (IX)	6,1	−4,7	−2,4	0,4	0	−2,6

conformation in the case of standard values of the angles and bond lengths the $H_7...{}^*H{-}CH_2$ distances in the case of the SCH_3 and OCH_3 groups are 1.6 and 1.1 Å, respectively. These values are considerably smaller than the sum of the van der Waals radii of two hydrogen atoms (2.4 Å). An increase in the $C_{ar}XCH_3$ angle or the length of the $C_{ar}X$ bond (X = O, S) as a consequence of steric hindrance entails a decrease in the average value of the shift of the C_7 signal to strong field because of polarization of the $C_7{-}H_7$ bond.



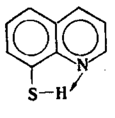
A



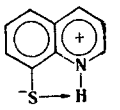
B

X = O, S

The difference in the $\Delta\delta_\alpha$ and $\Delta\delta_o$ values of the SH group for II and thiophenol ($\Delta\delta_\alpha$ = 2.2, $\Delta\delta_o$ = 0.4 ppm) is evidently due to the presence in the former of a strong intramolecular S–H ← N (form C) hydrogen bond (the latter is not disrupted either as the concentration of II is increased or in polar solvents [6]). The formation of the mesoionic form (D) of 8-mercaptoquinoline in $CDCl_3$ and CD_3OD [7] has virtually no effect on the ^{13}C chemical shifts of II (Table 1).



C



D

An intramolecular hydrogen bond may be the reason for the increase in the increments of the SH group ($\Delta\delta_\alpha$, $\Delta\delta_o$) in the II molecule relative to thiophenol, as well as for the change in the ratio of the ortho increments ($|\Delta\delta'_o|<|\Delta\delta''_o|$), while in S-methylquinolines [4] and in IV-VI and IX $|\Delta\delta'_o|>|\Delta\delta''_o|$ (Table 2). The effect of the contribution of an intramolecular hydrogen bond on the ^{13}C chemical shifts in the II molecule is similar in many respects to the changes in the ^{13}C chemical shifts in X (the mesoionic form) as compared with IV (the enol form). The formation of X is accompanied by a weak-field shift of the C_7 and C_8 signals and a strong-field shift of the C_9 signal (in the X molecule $|\Delta\delta'_o|<|\Delta\delta''_o|$, while in the IV molecule $|\Delta\delta'_o|>|\Delta\delta''_o|$). In contrast to II, the O–H ← N intramolecular hydrogen bond in the IV molecule is disrupted in concentrated solutions [8], and in the case of an OH group, just as for the OCH_3 group in V, $|\Delta\delta'_o|>|\Delta\delta''_o|$ and $\Delta\delta_\alpha < \Delta\delta_\alpha^B$ (Table 2).

Protonation of I gives rise to extremely significant changes in the ^{13}C chemical shifts (Table 1). However, the increments of the OH and OCH_3 groups in the IVo and Vo molecules differ little from those in the neutral forms of the IV and V molecules (Table 2). On the other hand, the increments of the SH and SCH_3 groups are decreased in IIo and IIIo as compared with II and III, and $|\Delta\delta'_o|<|\Delta\delta''_o|$. It is possible that this is associated with disruption of the conjugation of the SH and SCH_3 groups with the ring in the sterically strained fragment of the IIo and IIIo molecules. The sum of the van der Waals radii of the

TABLE 3. Coefficients of the Correlation Equations $\delta\ ^{13}C = aq_C + b$

Compounds	a	b	r
I—VI, VIII	211,4	126,8	0,95
I—VI, VIII, X	130,8	128,2	0,80
Io—Vo, IIa, IVa			
I—VI, VIII, X, Io—Vo IIa, IVa	176,2	127,3	0,92[a]
X, Io—Vo, IIa, IVa	102,4	128,7	0,74
X, Io—Vo, IIa, IVa	150,0	127,4	0,90[a]

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[a] The C_2 and C_9 atoms of Io-Vo and the C_2, C_7, and C_9 atoms of IIa, IVa, and X were excluded.

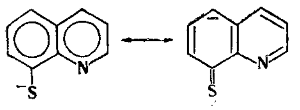
TABLE 4. Changes in the Shielding Parameters, Charges, and ^{13}C Chemical Shifts of the Ring Carbon Atoms in the Protonation of I and III

Atom No.	$\Delta\sigma_{AA}{}^{p}$	$\Delta\sigma_{AB}{}^{p}$	$\Delta\sigma^{d}$	$\Delta q \cdot 10^2$	$\Delta\delta$
		Quinoline			
C_2	−6,0	2,1	−0,7	9,1	−5,8
C_4	−7,5	−0,8	−0,8	9,8	13,0
C_7	−4,0	−1,3	−0,5	5,5	7,0
C_8	1,0	−0,7	0	−1,4	−9,0
C_9	−3,5	2,8	−0,4	5,4	−11,1
		8-Mercaptoquinoline			
C_2	−6,0	1,9	−0,8	9,2	−4,3
C_4	−7,5	−0,9	−0,8	9,8	12,3
C_7	−3,5	−1,5	−0,4	5,3	11,3
C_8	1,4	−0,9	0,1	−1,8	−6,1
C_9	−3,2	3,2	−0,4	4,8	−15,4

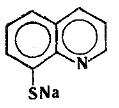
hydrogen (NH group) and sulfur atoms is 3.2 Å, while the H...S distance is only 2.5 Å (compare with IVo and Vo, in which the corresponding values are 2.6 and 2.5 Å).

In the case of the I-VI and VIII molecules the changes in the chemical shifts [13] are described satisfactorily by the changes in the total charges (q) on the carbon atoms. In the case of the protonated (Io-Vo) and anionic (IIa and IVa) forms these values correlate substantially more poorly (Table 3). In Io-Vo as compared with the corresponding neutral forms the signals of the C_2, C_8, and C_9 (to strong field) and C_4, C_6, and C_7 (to weak field) atoms undergo a substantial shift. Whereas the shifts of the signals of the C_4, C_6, C_7, and C_8 atoms generally are in the same direction as the change in q, the C_2 and C_9 signals are shifted in the opposite direction relative to the changes in q. This "anomalous character" of the behavior of the C_2 and C_9 atoms is explained by a decrease in the contribution of the paramagnetic component ($\sigma_{AB}{}^{p}$) to the shielding of these nuclei, and this affects the chemical shifts in a manner counter to the effect of an increase in the positive charge (Table 4).

The conversion of II and IV to anionic forms IIa and IVa is accompanied by a shift of the C_5 signal to strong field in the same direction as the change in q. However, the shifts of the C_7 and C_9 signals are not in agreement with the changes in q, σ_{AA}, and $\sigma_{AB}{}^{p}$. Variation of the geometry with allowance for the contribution of resonance structure F to ground state E does not improve the agreement between the experimental chemical shifts and the calculated values.



E F



G

The results of a calculation for the sodium salt of II (G) are also presented in Table 1. It turns out that this model describes the changes in the ^{13}C chemical shifts in the II molecule on passing from neutral solutions to alkaline solutions better than model E. The increase in the negative charge on C_7 and particularly on C_9 in the case of this model is not as clearly expressed as in the case of model E. The agreement between the changes in q and the chemical shifts of the C_2 and C_4 atoms is also improved. In accordance with this, it may be assumed that the sodium salts of II and IV (alkaline solutions) exist primarily in the unassociated state (as ion pairs). The shielding of the C_2, C_7, C_8, and C_9 nuclei in the IIa and IVa molecules (G) is also determined partially by the electrostatic fields of the charges on the sulfur and sodium atoms. Within the point-charge approximation, for example, the shifts of the C_7 signal induced by the charge of the sodium (+0.3 e) and sulfur (−0.3 e) atoms are 6 and −14 ppm, respectively. According to this, the principal reason for the weak-field shift of the C_7 and C_9 signals on passing from II and IV to IIa and IVa is the electrostatic field of the charge on the sodium atom. Taking into account the fact that the ^{13}C NMR spectra of IIa and IVa were obtained in an alkaline medium (pH ∿12), it may be assumed that the sulfur (oxygen) atom is surrounded by more than one sodium atom. This leads to an additional increase in the contribution of the electrostatic field of sodium to deshielding of the C_7 and C_9 atoms.

According to the results of the calculation, the changes in the charges on the atoms on passing from IV to X are determined by methylation of the nitrogen atom and the formation of a negative charge on the oxygen atom. The charges on the C_2 and C_9 atoms change only slightly, and the shift of their signals to weak field, which is close in magnitude in protonated form IVo, is due to a decrease in the order of the CN bonds. Methylation also caused a shift of the C_4 signal to weak field (an increase in the positive charge). In the X molecule, just as in IIa and IVa, the negative charge on the C_7 atom is greater than that in IV; however, the C_7 signal is shifted to weak field and, what is more, to a greater extent than in the case of the IVa molecule (Table 1). Whereas in the latter this shift is due to the effect of the electrostatic field of the sodium atom, in the X molecule, in which this effect is absent, it may be assumed that this is associated with weakening of the conjugation of the oxygen atom with the quinoline ring in the sterically strained fragment of the molecule (the $O...CH_3$ distance in X is 2.5 Å, while the sum of the van der Waals radii of the CH_3 group and the oxygen atom is 3.4 Å). As a consequence of this, the C_9 signal of X also undergoes a weak-field shift (relative to IV, the shift of the C_9 signal is only −4.1 ppm, as compared with −11.7 ppm in the case of the IVo molecule; see Table 1).

The nature of the solvent has an extremely substantial effect on the ^{13}C chemical shifts of X, in contrast, for example, to II (Table 1). On passing from $CDCl_3$ to CD_3OD the signals of the C_4, C_5, and C_7 atoms undergo a shift to weak field, while the C_8 signal undergoes a shift to strong field. This is evidently associated with the formation of an $O^- \rightarrow DOCD_3$ hydrogen bond, and the electronic structure of X approaches that of IVo. The latter is in good agreement with the hypsochromic shift of the long-wave absorption band in the electronic spectra of X on passing from solutions in slightly polar solvents to solvents that contain a hydroxy group [2].

The results of an analysis of the ^{13}C chemical shifts of various forms of 8-hydroxyquinoline and 8-mercaptoquinoline are of definite interest in connection with studies of the electronic structures of their chelate compounds on the basis of the ^{13}C NMR spectra. It is assumed that the ligands in the 8-mercaptoquinolinates of nontransition metals have a structure close to the structure of the thiol form, whereas in the chelate compounds of transition metals they have a structure that is close to that of the mesoionic form [1]. According to the data obtained, the ^{13}C chemical shifts of these ligands in chelate compounds will be determined not only by changes in the charge distribution but also by steric hindrance (IIo and IIIo), the electrostatic effect of the residual charge on the metal atom and the negative charge on the sulfur atom (IIa and IVa), changes in the bond order (Io-Vo), and the effects of the solvent (X). The combined influence of these effects determines the chemical shifts of the C_2, C_7, C_8, and C_9 atoms, and this hinders their use for studies of the charge distribution in these chelate compounds.

To this end one can use the changes in the chemical shifts of the C_4 and C_5 atoms. The latter are determined principally by the changes in the charges on the C_4 and C_5 atoms as a consequence of the formation of a bond with the nitrogen atom (Io-Vo and X) and the presence of a negative charge on the sulfur atom (IIa and IVa), respectively.

EXPERIMENTAL

The ^{13}C NMR spectra of 20% $CDCl_3$ solutions of the compounds containing cyclohexane (the internal standard) at room temperature were obtained with a Brüker WH-90 spectrometer (22.63 MHz) under pulse conditions (with 5 μsec pulses). The error in the shift on the δ scale from tetramethylsilane (with a computer memory of 4 K and a scanning width of 6000 Hz) was ±0.1 ppm. The spectra without decoupling of the protons were recorded at a scanning width of 1200 Hz.

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^{13}C NMR SPECTRA OF PROTONATED S-METHYLQUINOLINES

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The signals in the ^{13}C NMR spectra of protonated 2-, 3-, 4-, 5-, 6-, and 8-S-methylquinolines in solution in 6 N DCl were assigned. The changes in the ^{13}C chemical shifts relative to the neutral molecules were compared with the results of calculations within the CNDO/2 approximation. It is shown that when the molecules are protonated, the shift of the ^{13}C signals is due to changes in the charges and the paramagnetic components of shielding of the nuclei.

The ^{13}C NMR spectra, the increments of the substituents, and the charge distribution in S-methylquinolines were examined in [1]. In the present communication data from the ^{13}C NMR spectra of the cationic forms of quinoline (I) [2] and its 2-S-methyl (II), 3-S-methyl (III), 4-S-methyl (IV), 5-S-methyl (V), 6-S-methyl (VI), and 8-S-methyl (VII) [2] derivatives are presented in order to ascertain the changes in the electronic structure and the character of the coupling of the substituent with the quinoline ring when the nitrogen atom is protonated. The signals were assigned on the basis of the spectra without proton decoupling or with extraresonance suppression of the spin—spin coupling. The ^{13}C chemical shifts of I-VII are presented in Table 1. In Table 2 the increments of the SCH_3 group are compared with the values in the neutral forms of these compounds and the changes in the total charge (Δq) on the atoms and the paramagnetic ($\sigma_{AA}{}^{P}$, $\sigma_{AB}{}^{P}$) and diamagnetic (σ^{d}) components of shielding of the nuclei.

As in the case of quinoline [2], the protonation of S-methylquinolines is accompanied by a shift of the C_2 and C_9 signals to strong field. This is associated with a decrease in the contribution of the $\sigma_{AB}{}^{P}$ component to shielding of these nuclei because of a decrease in the order of the CN bond. The latter acts counter to the effect of an increase in the positive charge on these carbon atoms (Table 2). In the case of IV and V the shifts of the C_5 and C_4 signals, respectively, to strong field because of steric hindrance (the γ effect) are similar to the shifts for the neutral forms of these compounds.

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