^{13}C NMR SPECTRA OF 7-SUBSTITUTED 8-MERCAPTOQUINOLINES

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The ^{13}C NMR spectra of 7-substituted [7-CH_3, 2,7-$(CH_3)_2$, 7-Cl, 7-Br, and 7-SCH_3] 8-mercaptoquinolines and 8-methylmercaptoquinolines were examined. It is shown that the changes in the ^{13}C chemical shifts of the quinoline ring in the spectra of 7-substituted 8-mercaptoquinolines are in good agreement with the additive contribution of the increments of the substituents, i.e., their conjugation with the ring is not disrupted. The conjugation of the SCH_3 group with the quinoline ring in 7-substituted 8-methylmercaptoquinolines is disrupted as a consequence of steric hindrance, and this leads to a decrease in the increments of this group. The data obtained are compared with the results of a calculation within the CNDO/2 approximation.

Numerous studies of derivatives of 8-mercaptoquinoline have been made in connection with the analytical value of this reagent. 7-Substituted 8-mercaptoquinolines, the physicochemical and analytical properties of which differ markedly from those of other substituted 8-mercaptoquinolines [1-3] because of steric hindrance, are extremely unusual compounds in this series. In the present research in order to ascertain the changes in the electronic structures because of steric strain in the molecules of these compounds we examined the ^{13}C NMR spectra of the 7-methyl (I), 2,7-dimethyl (II), 7-chloro (III), 7-bromo (IV), and 7-methylmercapto (V) derivatives of 8-methylmercaptoquinoline and 8-mercaptoquinoline (VI-X, respectively). The increments of the substituents in the 7 position of the quinoline ring were estimated from the ^{13}C NMR spectra of 7-methyl- (XI), 2,7-dimethyl- (XII), 7-chloro- (XIII), and 7-bromoquinoline (XIV). The characteristics of the ^{13}C spectra of 7-methylmercaptoquinoline (XV), 8-methylmercaptoquinoline (XVI), 8-mercaptoquinoline (XVII), and quinoline (XVIII) are presented in [4, 5].

The chemical shifts of the ^{13}C signals, the assignment of which was made on the basis of the spectra without proton decoupling (with the Overhauser nuclear effect) or with extraresonance suppression of the ^{13}C—^{1}H spin-spin coupling, are presented in Table 1. The increments of the substituents ($\Delta\delta$) are presented in Table 2, while the contributions of the substituents to the ^{13}C chemical shifts of I-X are compared in Table 3 with the values calculated by an additive scheme. To estimate the effect of ortho substitution of XVI and XVII on the conjugation of the substituents with the quinoline ring in the 7 and 8 positions (I-X) we used the changes in the ^{13}C chemical shifts of the C_6, C_{10}, C_5, and C_9 atoms, respectively (the meta positions relative to C_8 and C_7, respectively).

The ^{13}C chemical shifts in the spectra of VI-X are in satisfactory agreement with the values expected in the case of exocyclic substitution of XVIII, i.e., ortho substitution of XVII has virtually no effect on the conjugation of the substituents with the ring. A certain decrease in $\Delta\delta$ as compared with the value calculated from the increments of the substituents is noticeable only for the C_7 atom (the additional shift to strong field is ~2 ppm). A shift of this sort is also observed in the spectra of o-substituted phenols, thiophenols, and anilines [6]. The reason for this in the VI and VII molecules is steric hindrance (polarization of the CH_3 group as a consequence of a van der Waals interaction). A similar shift in the spectra of VIII-X is evidently due to polarization of the C_{ar}—X bond (X = Cl,

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TABLE 1. ^{13}C Chemical Shifts (δ, ppm)[a] of I-XVIII

Atom No.	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV	XV	XVI	XVII	XVIII
C_2	150,9	159,2	151,4	151,3	151,2	150,0	157,8	150,2	150,1	149,8	150,7	158,9	151,6	151,7	151,2	149,4	149,7	150,7
C_3	121,4	121,5	121,8	121,9	120,4	121,0	121,3	121,8	121,9	121,2	120,7	121,4	121,6	121,8	120,7	122,2	122,0	121,6
C_4	137,1	137,1	137,2	137,3	136,8	137,6	137,0	137,2	137,2	137,4	135,9	136,0	136,0	136,2	136,1	136,7	137,2	136,4
C_5	128,6	127,6	129,1	129,3	129,0	123,6	122,8	124,5	124,7	124,1	127,9	127,6	128,8	129,5	128,2	123,9	124,9	128,4
C_6	130,3	128,8	128,6	131,4	122,6	129,8	128,4	127,9	130,6	126,6	129,0	128,4	127,7	130,4	126,4	127,2	126,9	127,0
C_7	144,2	143,3	140,7	131,4	147,5	133,7	134,9	131,2	121,2	137,2	139,7	139,7	135,4	123,9	141,9	123,2	127,4	129,9
C_8	133,6	134,3	135,4	138,3	131,0	135,6	133,5	135,3	137,9	128,8	129,0	128,1	129,4	132,3	123,7	140,6	135,4	129,9
C_9	149,1	148,6	149,3	149,2	148,7	143,9	142,3	143,8	143,8	143,8	149,0	148,7	148,9	149,3	149,4	145,8	144,1	148,8
C_{10}	128,2	126,2	127,9	128,3	126,4	127,5	125,1	127,0	127,1	126,4	127,4	125,0	126,9	127,2	126,4	128,5	129,1	128,8
CH_3	22,8[b]	23,0[b] 26,3[c]				22,2[b]	22,1[b] 25,5[c]				21,2[b]	22,2[b] 25,7[c]						
SCH_3	19,8[d]	20,2[d]	19,8[d]	20,3[d]	19,4[d] 16,4[e]					17,4[e]					15,5[e]	14,6[d]		

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[a] Relative to tetramethylsilane. [b] For the CH_3 group in the 7 position. [c] For the CH_3 group in the 2 position. [d] For the SCH_3 group in the 8 position. [e] For the SCH_3 group in the 7 position.

TABLE 2. Increments of the Substituents in XI-XVII

Substituent (compound)		$\Delta\delta_\alpha$	$\Delta\delta'_o$ [a]	$\Delta\delta''_o$	$\Delta\delta'_m$	$\Delta\delta''_m$	$\Delta\delta_p$
7-CH_3	(XI)	9,8	2,0	−0,9	−0,5	0,2	−1,4
7-CH_3	(XII)[b]	10,6	3,0	−0,6	−0,3	0,8	−1,4
7-Cl	(XIII)	5,5	0,7	−0,5	0,4	0,1	−1,9
7-Br	(XIV)	−6,0	3,4	2,4	1,1	0,5	−1,6
7-SCH_3	(XV)	12,0	−0,6	−6,2	−0,2	0,6	−2,4
8-SCH_3	(XVI)	10,7	−6,7	−3,0	0,2	−0,3	−4,5
8-SH	(XVII)	5,5	−2,5	−4,7	−0,1	0,3	−3,5

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[a] The $\Delta\delta'_o$, $\Delta\delta''_o$, $\Delta\delta'_м$, and $\Delta\delta''_м$ values are the increments of the substituents attached to the C_6, C_8, C_5, and C_9 atoms in XI-XV and to the C_7, C_9, C_6, and C_{10} atoms in XVI-XVII, respectively. [b] Relative to 2-methylquinoline.

TABLE 3. Experimental (Calculated) Changes in the ^{13}C Chemical Shifts of Quinoline upon Substitution

Substituent (compound)	C_8	C_7	C_6	C_5	C_9	C_{10}
8-(Methylthio)quinoline:						
7-CH_3 (I)	3,7 (9,8)	14,3 (3,1)	3,3 (2,2)	0,2 (−5,0)	0,3 (−2,8)	−0,6 (−1,7)
2-CH_3, 7-CH_3 (II)	5,6 (10,1)	14,2 (3,9)	3,4 (3,2)	0,3 (−4,8)	0,7 (−2,2)	−0,2 (−1,7)
7-Cl (III)	5,5 (10,2)	10,8 (−1,2)	1,6 (0,9)	0,7 (−4,1)	0,5 (−2,9)	−0,9 (−2,2)
7-Br (IV)	8,4 (13,1)	1,5 (−12,7)	4,4 (3,6)	0,9 (−3,4)	0,4 (−2,5)	−0,5 (−1,9)
7-SCH_3 (V)	1,1 (4,5)	17,6 (5,3)	−4,4 (−0,4)	0,6 (−4,7)	−0,1 (−2,4)	−2,4 (−2,7)
8-Mercaptoquinoline:						
7-CH_3 (VI)	3,8 (4,6)	5,7 (7,3)	2,8 (1,9)	−4,8 (−4,0)	−4,9 (−4,5)	−1,3 (−1,1)
2-CH_3, 7-CH_3 (VII)	4,8 (4,9)	5,8 (8,1)	3,0 (2,9)	−4,5 (−3,8)	−5,6 (−3,9)	−1,3 (−1,1)
7-Cl (VIII)	5,4 (5,0)	1,3 (3,0)	0,9 (0,6)	−3,9 (−3,1)	−5,0 (−4,6)	−1,8 (−1,6)
7-Br (IX)	8,0 (7,9)	−8,8 (−8,5)	3,6 (3,3)	−3,7 (−2,4)	−5,0 (−4,2)	−1,7 (−1,3)
7-SCH_3 (X)	−1,1 (−0,7)	7,3 (9,5)	−0,4 (−0,7)	−4,3 (−3,7)	−5,0 (−4,1)	−2,4 (−2,1)

Br, or SCH_3) by the dipole of the CSH group. In addition, the effect of the polar C_{ar}—X group in the VI-X molecules on the C_8 chemical shift is not expressed so distinctly. Whereas the C_8 signal undergoes an additional shift of 0.8 ppm to strong field in the case of VI, in the case of VII-X it virtually coincides with the calculated value (Table 3). In these compounds, in addition to the contribution of the substituents to the ^{13}C chemical shift, one must also evidently take into account the effect of the intramolecular hydrogen bond [7]. In the case of the VII molecule it was noted that the signals of the C_5 (0.7 ppm) and C_9 (1.7 ppm) atoms are shifted additionally to strong field (Table 3); this may be associated with an increase in the strength of the intramolecular hydrogen bond as compared with the XVII molecule (the increments of the SH group in the XVII molecule already contain a contribution of the $S—H \rightarrow N$ intramolecular hydrogen bond to the ^{13}C chemical shift). According to [5], the latter leads to a shift of the C_8 signal to weak field, i.e., the effect of polarization of the C_{ar}—S bond on the ortho substituent and the effect of the intramolecular hydrogen bond act in opposite directions and are evidently virtually compensated in VII (just as in VIII-X). In VI the effect of the intramolecular hydrogen bond on the ^{13}C chemical shift of the quinoline ring is expressed more weakly (see the $\Delta\delta$ values for the C_8 and C_9 signals in Table 3). The increase in the strength of the intramolecular hydrogen bond in the VII molecule as compared with VI cannot be associated with the inductive and mesomeric effects of the CH_3 group in the 2 position of the quinoline ring. It might be assumed that the strengthening in this case is due to deformation of the unshared pair of electrons of the nitrogen atom as a consequence of electron—electron repulsion of it and the CH_3 group.

In I-V the $\Delta\delta'_o$ and $\Delta\delta_n$ values of the substituents in the 7 position of the quinoline ring differ little from the values for the XI-XV molecules (except for the $\Delta\delta'_o$ value of the SCH_3 group in V), whereas the $\Delta\delta''_o$ and $\Delta\delta_n$ values of the SCH_3 group are significantly lower (−0.7-0.4 and −0.2-0.8 ppm, respectively) as compared with the values for XVI (Tables 2 and 3). The latter is a consequence of conjugation of the SCH_3 group with the ring in the sterically strained fragment of the I-V molecules. In V and X the trans configuration of the SCH_3 group relative to the substituent in the 8 position is determined by steric hindrance. In X the polarization of the C_6-H_6 bond of the methyl group as a consequence of a van der Waals interaction remains virtually the same as in XV. In the V molecule the influence of this effect on the chemical shift of the C_6 atom is substantially greater because of the bulkier substituent in the 8 position. Proceeding from the $\Delta\delta_\alpha$ and $\Delta\delta''_o$ values of the substitutents in XI-XV, the conjugation of which with the ring in I-V is virtually undisrupted, the $\Delta\delta_\alpha$ and $\Delta\delta'_o$ values of the SCH_3 group in I-V are 4.6-7.3 and 3.6-5.6 ppm, respectively. These increments, like the $\Delta\delta''_o$ and $\Delta\delta_n$ increments of the SCH_3 group, differ substantially in I-V from those in XVI (Table 2).

According to the results of a calculation within the CNDO/2 approximation, the shielding of the C_5, C_7, and C_9 nuclei in I and V decreases as compared with the corresponding VI and X, while the shielding of the C_8 nucleus increases (Fig. 1). This is in satisfactory agreement with the changes in the ^{13}C chemical shifts (Table 1). The certain contribution to the weak-field shift of the C_7 signal in the I-V molecules, in addition to a decrease in the electron density, also introduces an increase in the σ_{AB}^p component of the shielding. For example, according to the results of the calculation, the change in the σ_{AB}^p component of the C_7 atom is 1.2 ppm on passing from V to X. As a consequence of disruption of the conjugation of the SCH_3 group with the quinoline ring in the I-V molecules, the order of the $C_{ar}S$ bond (and the corresponding σ_{AB}^p value) decreases. This, together with the increase in the electron density on the C_8 atom, is responsible for the shift of the C_8 signal to strong field with respect to VI-X (in V, for example, the contribution of σ_{AB}^p to the shielding of the C_8 nucleus is 3 ppm greater than in X).

Thus, it follows from the results of the calculation and the ^{13}C NMR spectra that the changes in the ^{13}C chemical shifts of 7-substituted 8-(methylthio)quinolines as compared with the chemical shifts of the corresponding derivatives of 8-mercaptoquinoline are associated primarily with the changes in the charges on the atoms because of disruption of the conjugation of the SCH_3 group with the quinoline ring. This disruption is responsible to a great extent for the changes in the chemical shifts and the charges on the carbon atoms of the benzene ring and has virtually no effect on the corresponding parameters of the C_2, C_3, and C_4 atoms.

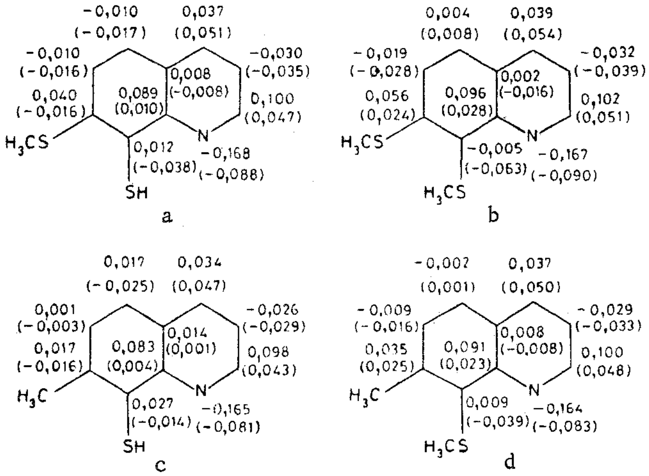

Fig. 1. Distribution of the overall (π-electron) density in the 7-(methylthio)- (a) and 7-methyl-8-mercaptoquinoline (c) and 7-(methylthio)- (b) and 7-methyl-8-methylquinoline (d) molecules.

EXPERIMENTAL

The ^{13}C NMR spectra of 20% solutions of the compounds in $CDCl_3$ containing cyclohexane (as the internal standard) were obtained at room temperature with a WH-90 spectrometer with an operating frequency of 22.63 MHz. The spectra were recorded under pulse conditions with a pulse duration of 5 μsec. The error in the shift on the δ scale from tetramethylsilane (in the case of a computer memory of 4-kilobytes and a scanning range of 6000 Hz) was ± 0.1 ppm.

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BENZO[g]ISOQUINOLINIUM BENZOYLMETHYLIDS

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Stable benzo[g]isoquinolinium methylids were obtained from N-phenacylbenzo[g]isoquinolinium bromides and two of its benzene ring-substituted analogs. The first of these quaternary salts was converted to benzo[g]isoquinolinium dibenzoylmethylid. 3-Benzoyl-1,2-dicarbomethoxynaphth[2,3-g]indolizine was obtained from the same salt with dimethyl acetylenedicarboxylate (via a 1,3-dipolar cycloaddition reaction).

Having at our disposal a relatively simple method for the synthesis of benzo[g]isoquinolines [1], the chemistry of which has thus far been studied to only a limited extent, we attempted to ascertain the possibility of the synthesis of benzo[g]isoquinolinium benzoylmethylids from them.

In the present research we used the previously synthesized benzo[g]isoquinoline (I), as well as 8-methyl- and 7,8-dimethylbenzo[g]isoquinolines (II, III) [2]. Benzo[g]isoquinolines I and III were converted to quaternary salts, viz., 2-phenacyl- and 7,8-dimethyl-2-phenacylbenzo[g]isoquinolinium bromides (IV, V), in quantitative yields by reaction with bromoacetophenone. The ylids of these nitrogen-containing heterocyclic systems, viz., benzo[g]isoquinolinium benzoylmethylid (VI) and 7,8-dimethylbenzo[g]isoquinolinium benzoylmethylid (VIII), were obtained by treatment of these salts with a solution of potassium carbonate. 8-Methylbenzo[g]isoquinolinium methylid (VII) was similarly obtained without isolation of the corresponding quaternary salt. Benzo[g]isoquinolinium dibenzoylmethylid (IX) was obtained via the Schotten–Baumann reaction by benzoylation of quaternary salt IV.

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