^{1}H AND ^{13}C NMR SPECTRA OF 8-HYDROXYQUINOLINE

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The ^{1}H and ^{13}C NMR spectra of 8-hydroxyquinoline were analyzed. The assignment of the signals was established unambiguously by ^{13}C–{^{1}H} double-resonance experiments and investigation of the ^{13}C NMR spectrum without decoupling from the protons.

A joint study of the ^{1}H and ^{13}C NMR spectra of 8-hydroxyquinoline as compared with the spectrum of quinoline has made it possible to unambiguously establish the correct assignment of the signals in the proton spectrum and to eliminate the contradictions in the literature [1, 2]. The assignment of the signals in the ^{13}C NMR spectrum (Table 1) was made by comparison with quinoline [3]. The changes in the shifts ($\Delta\delta$) induced by the hydroxyl group are close to those observed on passing from naphthalene to 1-naphthol [4]: +22.84 and +23.36 for a carbon atom bearing a substituent, −18.36 and −16.99 for ortho-C, +0.91 and +0.06 for meta-C, −10.23 and −7.08 for para-C, −10.74 and −9.12 for 9-C, and +0.11 and +1.26 for 10-C. In the spectrum without irradiation of the protons we observed spin–spin coupling of 5-C with 4-H in the peri position ($J \sim 4$–5 Hz), which is characteristic for two-ring aromatic systems [4, 5]. The assignment of the PMR spectrum (Table 2) was accomplished by the ^{13}C–{^{1}H} double-resonance method proceeding from the established assignment of the ^{13}C NMR spectrum. The analysis of the ABC spectrum of the protons of the phenol ring was made by means of Spin Simulation and ITRCAL programs with Varian 620-L and BNC-12 minicomputers. The incorrect assignment of signals from 5-H and 7-H in [1] requires reconsideration of the conclusions drawn in it regarding the different dependences of these signals on the solvent. In addition, as in the case of unsubstituted quinoline [6], in the correct assignment the J_{ortho} value in the phenol ring of 8-hydroxyquinoline is greater for α,β protons than for the β,β protons ($J_{5,6} > J_{6,7}$).

TABLE 1. ^{13}C Chemical Shifts in the Spectra of Quinoline and 8-Hydroxyquinoline (in ppm) with Tetramethylsilane as the Internal Standard

C atom	Quinoline [3]	8-Hydroxyquinoline	$\Delta\delta=\delta_{8\text{-}OH\cdot X}-\delta_X$
C-2	150,89	148,23	−2,66
C-3	121,67	121,55	−0,12
C-4	136,12	136,33	+0,21
C-5	128,46	118,23	−10,23
C-6	126,95	127,86	+0,91
C-7	129,86	111,50	−18,36
C-8	130,50	153,34	+22,84
C-9	149,28	138,54	−10,74
C-10	128,89	129,00	+0,11

TABLE 2. Chemical Shifts and Spin–Spin Coupling Constants of the Protons of 8-Hydroxyquinoline

Solvent	δ, ppm						J, Hz					
	H-2	H-3	H-4	H-5	H-6	H-7	2–3	2–4	3–4	5–6	5–7	6–7
CCl_4	8,70	7,31	8,03	7,13	7,30	7,01	4,2	1,6	8,3	8,2	1,4	7,7
$(CD_3)_2SO$	8,84	7,53	8,31	7,39	7,43	7,09	4,0	1,6	8,4	8,3	1,0	7,8

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SPECTRAL LUMINESCENCE PROPERTIES OF 1- AND 2-ALKYL(CYCLOALKYL) DERIVATIVES OF BENZO[*f*]QUINOLINE

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The absorption and fluorescence spectra of alcohol solutions of 3-aryl-substituted benzo[*f*]-quinolines were investigated, and the fluorescence quantum yields were measured. It was established that the indicated compounds have intense absorption in the UV region and fluorescence at 350-450 nm. The fluorescence quantum yields range from 5 to 70%, depending on the substituents. The introduction of aromatic substituents in the 1 and 3 positions of benzo[*f*]quinoline ring raises the fluorescence quantum yields. A methyl group in the 2 position of the molecule leads to a decrease in the fluorescence quantum yield. Benzo[*f*]quinoline derivatives that contain a cyclopentene ring in the 1 and 2 positions fluoresce intensely (γ = 40-60%), while cyclohexene and cycloheptene condensed in the same positions cause a decrease in the fluorescence yield to 7-13%; this is associated with the three-dimensional structure of these molecules.

It is known that most of the organic luminophores that are in use have heterocyclic systems. The use of aryl-substituted pyrazolines, oxazoles, imidazoles, and other compounds as optical bleaches, fluorescent pigments, and the active substances of lasers [1] has served as an impetus for numerous new studies of the optical properties of complex organic molecules.

Little study has been devoted to the spectral luminescence characteristics of benzo[*f*]quinoline and its derivatives. The literature contains information regarding the existence of fluorescence in solutions of benzo-

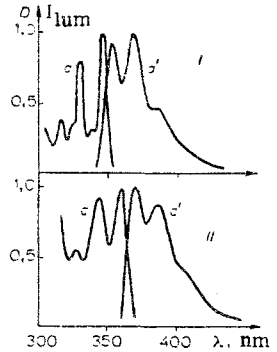

Fig. 1. Absorption (a) and fluorescence (a') spectra of alcohol solutions of benzo[*f*]quinoline (I) and 3-phenylbenzo[*f*]quinoline (II).

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