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PHOTOPHYSICAL BEHAVIOUR OF CHLOROQUINOLINES*

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The substituent and solvent effects on the luminescence spectra, quantum yields and the phosphorescence lifetimes of 2-, 4-, 6-, 7-chloroquinolines (n-ClQ) and 2,4- and 4,6-dichloroquinolines in ethanol and hydrocarbon matrices were investigated. The phosphorescence spectra of quinoline and four monochloroquinolines were recorded in the Shpolsky type matrices. The phosphorescence spectra of the chloroquinolines show the out-of-plane (skeletal and C-Cl) vibronic bands with the intensity dependent on the position of the Cl atom on the quinoline molecule. Possible spin-orbit coupling schemes for the internal heavy atom effects for the quinoline molecules substituted by the chlorine atoms are discussed. The internal heavy atom effects for the nonradiative transitions in the chloroquinolines are also position dependent. The decay constants of the singlet and triplet states of the n-ClQs show that the chlorine atom at the 2-position decreases the spin-orbit coupling between the $^1n\pi^*$ and $^3\pi\pi^*$ states relative to that in the quinoline molecule. Simultaneously, the substitution of the nitrogen atom into the aromatic naphthalene system decreases the influence of the heavy atom (Cl) relative to that in the chloronaphthalenes.

1. Introduction

The characteristic feature of naphthalene N-heterocyclics is close proximity of the $n\pi^*$ and $\pi\pi^*$ electronic states [1–5]. These electronic states are mixed by the out-of-plane vibrations as demonstrated for many N-heterocyclic compounds in the phosphorescence, fluorescence and absorption spectra [4–10]. Recently, Wassam and Lim [11, 12] showed that the out-of-plane modes involved in $n\pi^*$ and $\pi\pi^*$ mixing may have an important role in the radiationless transitions in azaaromatic hydrocarbons. For azaaromatics with $n\pi^*$ and $\pi\pi^*$ electronic states in close proximity, the internal conversion from S_1 may compete efficiently with the $S_1 \rightsquigarrow T$ intersystem crossing. The results of the model calculations

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[12] suggest the interpretation of the substituent effects, thermal effects and solvent effects generated by hydrogen bonding on the luminescence of azaaromatics.

The phosphorescence spectra of the aromatic hydrocarbons show the importance of the direct spin-orbit coupling and the vibronic spin-orbit coupling of the lowest triplet state and $^1\sigma\pi^*$ and $^1\pi\pi^*$ states [1]. Both routes involve $\sigma\pi^*$ or $\pi\sigma^*$ electronic states. The substitution of the heavy atoms (Cl, Br and I) into an aromatic hydrocarbon introduces new electronic states of the $\sigma\pi^*$ and $\pi\pi^*$ type. The spin–orbit coupling of the lowest triplet state for these states is responsible for the internal heavy atom effects [1, 13, 14]. The most significant dependences upon the heavy atom effects are the nuclear charge dependences [1]. The effect of the position of the heavy atom on the decays for the halosubstituted compounds is not so significant. Halonaphthalenes show little positional dependence on the triplet lifetime [15].

In the azaaromatic hydrocarbons the most important spin-orbit coupling route involves the direct spin-orbit coupling $^3\pi\pi^*$ and $^1n\pi^*$ states. [1, 3]. The influence of the chlorine atom on the photophysical processes in the chloroquinolines studied involves the typical substituent effects on the electronic states and on the internal heavy atom effects [16–19]. The quinoline molecule, which has the electronic states of the $n\pi^*$ and $\pi\pi^*$ type in close proximity, shows the significant positional dependence of the fluorescence and the phosphorescence quantum yields and the triplet lifetimes on the substitution. The acceleration of the photophysical processes by the substitution of the chlorine atom in azaaromatic compounds is smaller than that for aromatic hydrocarbons and shows the competition between different mechanisms of the spin-orbit mixing.

In this paper we compare the spectroscopic data, the phosphorescence spectra, and the lifetimes and the luminescence quantum yield data for some chloroquinolines.

2. *Experimental*

Preparation of Compounds. All the chloroquinolines investigated in the present study [(except for 2-chloroquinoline (2-ClQ) (Loba — Chemie)] were synthesised by methods previously described: 4-chloroquinoline (4-ClQ) [25], 6-chloroquinoline (6-ClQ) [26], 7-chloroquinoline (7-ClQ) [27], 2,4-dichloroquinoline (2,4-DClQ) [28] and 4,6-dichloroquinoline (4,6-DClQ) [29]. The compounds were purified by column chromatography (solids) using Woelm basic alumina or subjected to a fractional distillation (liquid) under reduced pressure (5 mm Hg). Additionally, the samples of the solid chloroquinolines were sublimed twice at 0.05 mm Hg or redistilled in a vacuum (7-ClQ) prior to the measurements. Ethanol (EtOH) and isooctane were distilled on the column, spectrograde *n*-hexane (Loba — Chemie) was used without further purification. For quantum yield determinations quinine sulphate standard was used.

Fig. 1 shows the experimental set up to determine the absorption coefficient at the excitation wavelength and the luminescence quantum yields at 95 K. The sample in the cylindrical pyrex tube in copper sample holder was excited by a 303 nm Hg line using an HBO-200 mercury lamp and a Double M3 COBRABID monochromator. The sample was cooled to 95 K and the transmission of the sample was determined for two wavelength of excita–

tion using the photomultiplier attached to the cryostat chamber. For the same sample, the luminescence spectra were recorded and compared with the luminescence of the standard. The luminescence was analysed using a SPM-2 monochromator Zeiss Jena quartz prism and an EMI 9558 B photomultiplier. The luminescence spectra were not corrected.

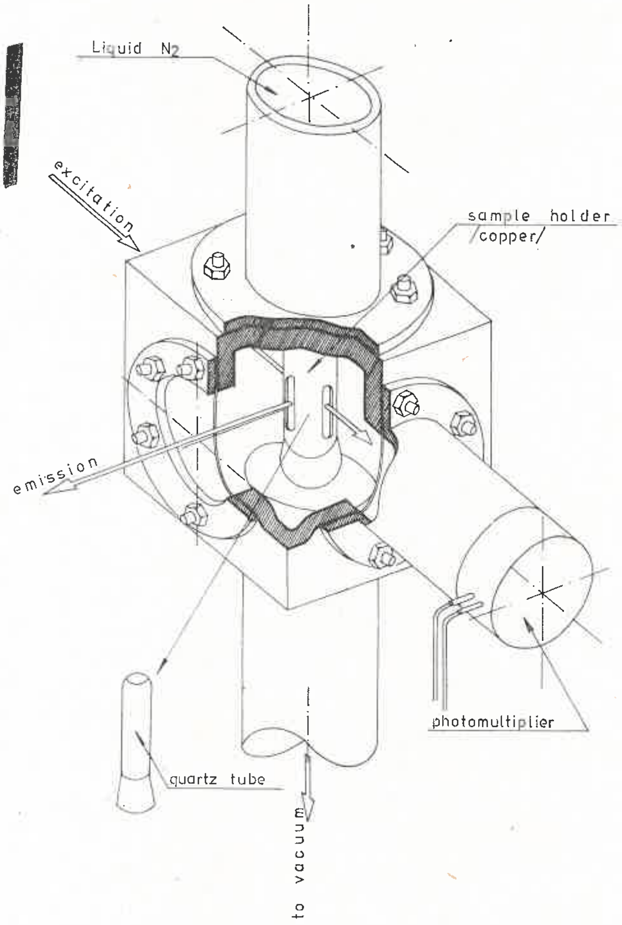


Fig. 1. The cryostat system for the determination of the luminescence quantum yields and absorption of solutions in organic glasses at ~95 K

The fluorescence and the phosphorescence spectra of the chloroquinolines are in the same spectral regions as those of naphthalene and quinoline. Thus, only a mean correction ratio was used for the correction of the Φ_{FS}/Φ_{PT} values of chloroquinolines. The mean correction factor was determined using the published quantum yield data for naphthalene and quinoline [20, 22]. For the triplet lifetime measurements the phosphorescence decay functions were recorded using a Hewlett Packard 1201A oscilloscope. The phosphorescence lifetimes were calculated using a computer programm to evaluate the moments of different orders of the decay function.

The phosphorescence spectra of the chloroquinolines were measured in Shpolsky type matrices (*n*-hexane and isooctane) at 77 K in thin pyrex tubes immersed directly in the liquid nitrogen in a transparent pyrex dewar. The phosphorescence spectra were measured using a Cary 82 Raman spectrometer for analysis and an HBO-200 mercury lamp and a Double M3 COBRABID monochromator for excitation (313 nm).

The spectral sensitivity factor for the Cary 82 spectrometer with an ITT-FW 130 photomultiplier was determined using the quinine sulphate standard [21]. The Cary 82 spectrometer was also used for the measurement of the Raman spectra of the chloroquinolines at room temperature using 488 nm and 514.5 nm lines from Ar^+ laser.

3. *Experimental results*

The energies of the $S_1(\pi\pi^*)$ and T_1 electronic states of the chloroquinolines in methylcyclohexane: isopentane (1 : 1), ethanol, *n*-hexane and isooctane are given in Table I. The S_1 energies were determined from the singlet–singlet absorption spectra. In hexane

TABLE I

Energies of the lowest S $(\pi\pi^*)$ and T electronic states of chloroquinolines

Molecule	E_S [cm^{-1}]	E_{T_1} [cm^{-1}]
quinoline	32000 *a*, 31860 *b*	21755, 21590 *c*, 21915 *d*
2-chloroquinoline	31390 *a*, 31430 *b*	22210, 22110, 21990, 21955, 21835 *c*, 22120 *a*
4-chloroquinoline	31040 *a*, 31620 *b*	21440 *d*, 21450 *a*
6-chloroquinoline	31140 *a*, 31250 *b*	21615, 21480, 21340 *c*, 21650 *a*
7-chloroquinoline	31210 *b*	21680, 21535 *c*
2,4-dichloroquinoline	31580 *a*, 31120 *b*	21640 *a*, 21730, 21705, 21600 *d*
4,6-dichloroquinoline	30620 *a*, 30810 *b*	21340 *a*, 21270, 21175 *d*

a — methylcyclohexane: isopentane (1 : 1), *b* — ethanol, *c* — hexane, *d* — isooctane. For crystalline matrices energies of different sites are given.

TABLE II

The luminescence quantum yields of chloroquinolines

Molecule	Φ_{PT} *b* 95 K	Φ_{FS}/Φ_{PT} *b* 77 K	Φ_{FS}/Φ_{PT} *a* 77 K	Φ_{FS}/Φ_{PT} *b* *n*-MeQ 77 K
2-chloroquinoline	0.35±20%	0.32±10%	0.22±10%	3.3
4-chloroquinoline	0.10	0.11	—	0.84
6-chloroquinoline	0.20	0.40	—	4.5
7-chloroquinoline	0.15	0.10	—	0.95
2,4-dichloroquinoline	0.12	0.20	0.03	—
4,6-dichloroquinoline	0.07	0.21	—	—

n-MeQ: 2-, 4-, 6-, and 7-methylquinoline, *a* — methylcyclohexane: isopentane, *b* — ethanol

TABLE III

The phosphorescence lifetimes τ_T [s] of chloroquinolines and methylquinolines at 77 K

Molecule	τ_T *b*	τ_T *c*	τ_T *d*	τ_T *e*	τ_T *n*-MeQ, *b*
quinoline	1.30 ± 0.05	0.86 ± 0.01	0.90 ± 0.01		
2-chloroquinoline *f*	0.77 ± 0.01	0.62 ± 0.02	0.62 ± 0.02	0.52 ± 0.01	1.42
4-chloroquinoline	0.40 ± 0.01	0.30 ± 0.01	0.29 ± 0.01	0.21 ± 0.01	1.52
6-chloroquinoline	0.26 ± 0.01	0.26 ± 0.02	0.26 ± 0.01	0.19 ± 0.01	1.05
7-chloroquinoline	0.31 ± 0.01	0.27 ± 0.01	0.28 ± 0.01	0.25 ± 0.01	1.35
2,4-dichloroquinoline	0.36 ± 0.01	0.32 ± 0.02	0.31 ± 0.01	0.24 ± 0.02	
4,6-dichloroquinoline	0.14 ± 0.01	0.16 ± 0.02	0.15 ± 0.02	0.12 ± 0.02	

* *n*-MeQ: 2-, 4-, 6-, and 7-methylquinoline, *b* — ethanol, *c* — hexane, *d* — isooctane, *e* — carbon tetrachloride, *f* — τ_T (in durene) = 0.42 ± 0.02 s.

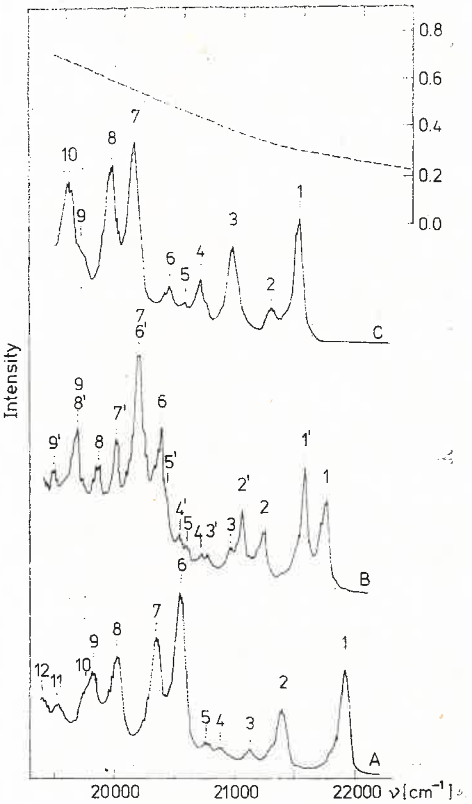


Fig. 2. The phosphorescence spectra of quinoline in isooctane *A* and *n*-hexane *B* and 4-chloroquinoline *C* in isooctane at 77 K (——— — spectral sensitivity of the analysing system)

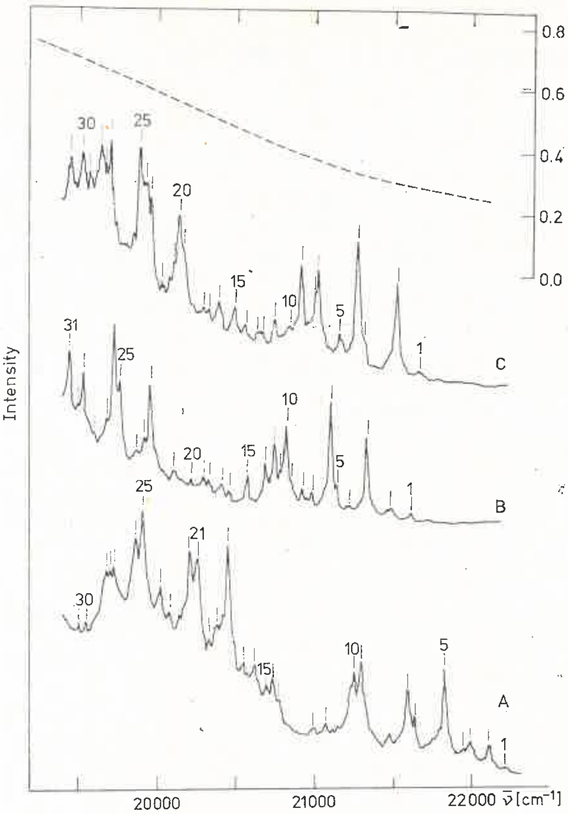


Fig. 3. The phosphorescence spectra of 2-chloroquinoline *A*, 6-chloroquinoline *B* and 7-chloroquinoline *C* in *n*-hexane at 77 K (——— — spectral sensitivity of the analysing system)

TABLE IV

Analysis of $T_1 \rightarrow S_0$ transition of quinoline in isooctane at 77 K

No	Band position	Intensity	$0_i - \bar{\nu}$	Possible assignment	Difference	Raman
1	21915 cm⁻¹	s	0_1			
2	21395	s	520	0_1 — 520	0	520 cm⁻¹
3	21125	w	790	785	+5	785
4	20890	w	1025	1037	−12	1037
5	20770	w	1145	1145	0	1145
6	20540	s	1375	1373	+2	1373
7	20345	s	1570	1572	−2	1572
8	20015	s	1900	520−1373	+7	
9	19820	s	2095			
10	19760	w	2155	785+1373	−3	
11	19525	m	2390	1037+1373	−20	
12	19400	w	2515	1145+1373	−3	
13	19190	w	2725	2×1373	−21	
14	18980	w	2935	1373+1572	−10	

and isooctane the phosphorescence spectra of the chloroquinolines and quinoline are the superpositions of the spectra resulting from different sites or groups of sites. The T_1 energies of the chloroquinolines for all sites which could be distinguished in our spectra are given in Table I.

The quantum yields of the phosphorescence of the chloroquinolines in ethanol were at 95 K, and the fluorescence to the phosphorescence quantum yield ratios are given in Table II. For the quantum yield determinations the chloroquinoline concentrations were about 2×10^{-5} M. A rough estimate of the phosphorescence quantum yields of the chloroquinolines in M/I showed that they are smaller than in ethanol. The photophysical data for methylquinolines published by Janîc [23], are included for easy comparison in the

TABLE V

Analysis of $T_1 \rightarrow S_0$ transition of quinoline in hexane at 77 K

No	Band position	Intensity	$0_i - \bar{\nu}$	Possible assignment	Difference	Raman
1	21755 cm^{-1}	s	0_1			
1′	21590	s	$0_{1'}$			
2	21240	s	515	0_1 — 520	−5	520
2′	21060	s	530	$0_{1'}$— 520	+10	
3	20960	m	795	0_1 — 785	+10	785
3′	20780	m	810	$0_{1'}$— 785	+25	
4	20725	m	1030	0_1 —1037	− 7	1037
4′	20545	m	1045	$0_{1'}$—1037	+ 8	
5	20605	m	1150	0_1 —1145	+ 5	1145
5′	20430	vw	1160	$0_{1'}$—1145	+15	
6	20380	s	1375	0_1 —1373	+ 2	1373
6′ 7	20195	s	1395 1395	0_1 —1572, $0_{1'}$—1373	−12, +22	1572
7′	20005	s	1585	$0_{1'}$—1572	+13	
8	19855	m	1900	0_1 —1373—520	+ 7	
8′	19670	s	1920	$0_{1'}$— 520—1373	+27	

TABLE VI

Analysis of $T_1 \rightarrow S_0$ transition of 4-chloroquinoline in isooctane at 77 K

No	Band position	Intensity	$0_i - \bar{\nu}$	Possible assignment	Difference	Raman
1	21440 cm^{-1}	s	0_1			
2	21205	w	235	220	+15	220
3	20890	s	550	544	+ 6	544
4	20610	m	830	822	+ 8	822
5	20480	w	960			
6	20350	m	1090	2×544	+ 2	
7	20070	s	1370	1360	+10	1360
8	19880	s	1560	1557	+ 3	1557
9	19630	w	1810	220+1557	+33	
10	19520	w	1920	544+1360	+16	

TABLE VII

Analysis of $T_1 \rightarrow S_0$ transition of 2-chloroquinoline in hexane at 77 K

No	Band position	Intensity	$0_i - \bar{\nu}$	Possible assignment	Difference	Raman
1	2	3	4	5	6	7
1	22210 cm^{-1}	vw		0_1		
2	22110	m		0_2		
3	21990	m		0_3		
4	21955	vw		0_4		
5	21835	s		0^5		
6	21640	w	0_5-195	0_5-195	0	195
7	21590	s	245	0_5-229	+16	229
8	21475	w		0_3-527	−12	527
9	21295	s	540	0_5-527	+13	
10	21250	s	585	0_5-597	−12	597
11	21070	w	765	0_5-772	− 7	772
12	21985	w	850	0_5-852	− 2	852
13	20770	w	1065	$0_5-2\times 527$	+11	
14	20735	m		0_2-1380	− 5	1380
15	20700	w	1135	0_5-1135	0	1135
16	20620	m		0_3-1380	−10	
17	20550	m	1285	$0_5-1295, 0_5-527-772$	0, −14	1295
18	20455	s	1380	0_5-1380	0	
19	20380	w		$0_3-229-1380$	+ 1	
20	20330	w	1505	0_5-1500	+ 5	1500
21	20260	s	1575	0_5-1566 (1578)	+9, −3	1566
22	20205	s	1630	$0_5-229-1380$	+21	1578
23	20080	m	1755	$0_3-527-1380$	+ 3	
24	20020	m	1815	$0_5-229-1566$ (1578)	+ 8	
25	19910	s	1925	$0_5-527-1380$	+18	
26	19870	w	1965	$0_5-597-1380$	−12	
27	19730	m	2105	$0_5-527-1566$ (1578)	−12(0)	
28	19705	m	2130	$0_5-229-527-1380$	− 6	
29	19685	m	2150	$0_5-772-1380$	− 2	
30	19550	w	2285	$0_5-2\times 527-1380$	+ 6	
31	19500	w	2335	$0_5-772-1566$ (1578)	− 3 (−15)	

last column of Table II. In experiments with quinoline and 2-ClQ in ethanol we found that the temperature dependences of the photophysical processes between 77 K and 95 K are insignificant.

The triplet lifetimes determined from the phosphorescence decay curves after cutting off the steady state excitation are given in Table III. The lifetime measurements were performed on solutions containing 10^{-3} M of the solute in ethanol, *n*-hexane, isooctane and CCl_4. In Table III the triplet lifetimes of the methylquinolines and quinoline [23] are also included. The phosphorescence spectra of quinoline and the chloroquinolines were investigated in ethanol, M/I, *n*-hexane, and isooctane at a concentration of 10^{-3} M. In ethanol glass the phosphorescence spectra were obtained in Shpolsky type matrices. In

TABLE VIII

Analysis of $T_1 \rightarrow S_0$ transition of 6-chloroquinoline in hexane at 77 K

No	Band position	Intensity	$0_i - \bar{\nu}$	Possible assignment	Difference	Raman
1	2	3	4	5	6	7
1	21515 cm^{-1}	w		0_1		
2	21480	w		0_2		
3	21340	s		0_3		
4	21220	w	$0_3 - 120$			
5	21145	w	195	$0_3 - 200$	− 5	200
6	21105	s	235	228	+ 7	228
7	20985	m	355	359	− 4	359
8	20920	m	420	419	+ 1	419
9	20860	w	480	481	− 1	481
10	20825	s	515	512	− 3	512
11	20800	vw	540	535	− 5	535
12	20780	vw	560	$0_1 - 200 - 535$	0	
13	20745	m	595	$0_3 - 609$	−14	609
14	20690	m	650	646	+ 4	646
15	20575	m	765	770	− 5	770
16	20460	w	880	888	−8	888
17	20410	w	930			
18	20335	w	1005	359−646	0	
19	20295	w	1045	1036	+9	1036
20	20215	w	1125	1120	−5	1120
21	20105	w	1235			
22	19960	s	1380	1378	−2	1378
23	19915	w	1425	1424	−1	1424
24	19870	w	1470	1480	+10	1480
25	19765	m	1575	1568	−7	1568
26	19730	s	1610	228−1378	−4	
27	19685	w	1655	228−1424	−3	
28	19605	vw	1735	359−1378	−2	
29	19540	m	1800	228−1568	−4	
30	19510	vw	1830	359−1480	+9	
31	19450	m	1890	521−1378	0	

hexane and isooctane matrices the chloroquinolines occupy several groups of the sites. While 4-chloroquinoline well resolved phosphorescence spectrum in isooctane, the chloroquinolines containing the chlorine atoms in positions 2, 6, and 7 gave narrow quasilinear spectra in *n*-hexane. For quinoline in *n*-hexane we found two groups of the sites separated by 180 cm^{-1} and populated to a similar extent. The phosphorescence spectra of the monochloroquinolines and quinoline in *n*-hexane and isooctane are shown in Figs 2 and 3. The sensitivity function of a Cary 82 spectrometer is also given in Figs 2 and 3. Usually 5 cm^{-1} slitwidths were used during recording of the quasilinear phosphorescence spectra. The noise in the phosphorescence spectra given in Figs 2 and 3 is mainly dependent on the stability of our excitation system. We found for 2-ClQ in hexane some photo-

TABLE IX

Analysis of $T_1 \rightarrow S_0$ transition of 7-chloroquinoline in hexane at 77 K

No	Band position	Intensity	$0_i - \bar{\nu}$	Possible assignment	Difference	Raman
1	2	3	4	5	6	7
1	21680 cm^{-1}	w		0_1		
2	21535	s		0_2		
3	21330	vw	0_2-205	0_2-197	+8	197
4	21290	s	245	238	+7	238
5	21170	m	365	356	+9	356
6	21060	vw	475	480	−5	480
7	21030	s	505			
8	21010	w	525	528	−3	528
9	20925	s	610	607	+3	607
10	20855	vw	680	658	+22	658
11	20755	m	780	769	+11	769
12	20685	w	850	841	+9	841
13	20635	w	900	910	−10	910
14	20565	w	970	2×480	+10	
15	20505	m	1030	1027	+3	1027
16	20400	m	1135	1130	+5	1130
17	20335	w	1200	1190, 2×607	+10, −14	1190
18	20295	w	1240	0_1-1382	+3	
19	20180	vw	1355	0_2-1360	−5	1360
20	20150	s	1385	1382	+3	1382
21	20100	vw	1435	1436	−1	1436
22	20040	w	1495	1495	0	1495
23	19965	w	1570	1567	+3	1567
24	19940	w	1595	1595	0	1595
25	19900	s	1635	238−1382	+15	
26	19715	s	1820	238−1567	+15	
27	19690	m	1845	238−1595	+12	
28	19655	m	1880	505−1382	−7	
29	19585	m	1950	607−1360	−17	
30	19540	m	1995	607−1382	+6	
31	19445	m	2090	505−1567	+18	

chemical changes under very intense excitation. For the purposes of comparison, we present the phosphorescence spectra of quinoline and the monochloroquinolines in the range of 19500–22000 cm^{-1}. The total phosphorescence spectra for all the chloroquinolines studied contain long progressions in frequencies of 1360–1578 cm^{-1}.

Fig. 2 shows the phosphorescence spectra of quinoline in isooctane *A* and *n*-hexane *B* and 4-ClQ in isooctane *C* at 77 K. The phosphorescence spectra of 2-ClQ, 6-ClQ and 7-ClQ in the hexane matrix are given in Fig. 3 as *A*, *B*, and *C*, respectively. The analysis of the phosphorescence spectra of the chloroquinolines, based on the Raman frequencies, are given in Tables IV–IX. A possible assignment of the presented parts of the phosphorescence spectra of quinoline in isooctane and *n*-hexane are given in Tables IV and V.

The phosphorescence spectra of 2-ClQ and 6-ClQ (Fig. 3, *A* and *B*) in *n*-hexane are analysed in Tables VII and VIII. The corresponding analysis of the phosphorescence spectrum of 7-ClQ in *n*-hexane is given in Table IX. The phosphorescence spectra of dichloroquinolines (2,4-DClQ and 4,6-DClQ) in *n*-hexane and isooctane show significant vibronic activity and are relatively broad.

The phosphorescence spectra in Shpolsky type matrices

The phosphorescence spectra of quinoline have been studied by several investigators [3–6, 10]. The emission was ascribed to the $^3\pi\pi^* \rightarrow {}^1A$ transition. This assignment was derived from such experimental evidence as the values of the electronic energy, phosphorescence lifetime, and structure of the phosphorescence spectra compared to those of naphthalene and quinoxaline. The polarization phosphorescence spectra of quinoline in glasses, durene and biphenyl showed weak vibronic out-of-plane bands involving C-H bending [3, 6]. In the quinoxaline phosphorescence spectra several vibronic bands due to a_2(475, 635 cm^{-1}) and b_1(747, 880 cm^{-1}) vibrations are active [17–19]. In the phosphorescence spectrum of 2,3-dichloroquinoxaline, Ishi et al. [17] found the activity of the b_1(375, 495^{-1}) and a_2(275, 880 cm^{-1}) vibrational modes. They found an increase in the intensity of the a_2 vibronic bands as the characteristic feature for the internal heavy atom effect.

Halosubstitution of N-heterocyclics generally causes a red shift of the $\pi\pi^*$ electronic states and a blue shift in the $n\pi^*$ electronic states [17]. In addition to the energy level shifts, substitution by halogens introduces new $\sigma\pi^*$, $\pi\sigma^*$ electronic states with the participation of the atomic orbitals centered on the heavy atoms. This increases the direct spin-orbit coupling between the lowest triplet and single states [1]. In the phosphorescence spectra of the halosubstituted naphthalenes, the direct spin-orbit coupling and second order coupling involving spin-orbit coupling and mixing of the $\pi\pi^*$ and $\sigma\pi^*$, $\pi\sigma^*$ states by the out-of-plane vibrations of the heavy atom are of a similar order of magnitude [1]. For the chloroquinolines the contribution involving the out-of-plane modes ($\sim$250 cm^{-1}) is dependent on the position of the chlorine atom. The strongest vibronic contributions induced by the heavy atoms were found for 6-ClQ and 7-ClQ. The vibronic activity of the out-of-plane C-H vibrations (770–830 cm^{-1}) involved in $n\pi^*$–$\pi\pi^*$ mixing in the quinoline derivatives is relatively small (less than for quinoxaline), but may be easily detected in our phosphorescence spectra.

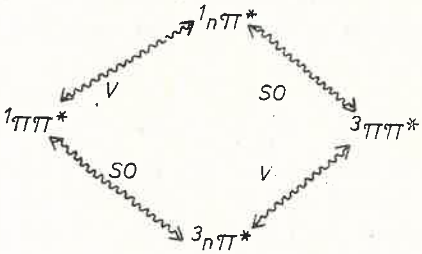
The spin-orbit coupling schemes for the $T_1 \rightarrow S_0$ transition in the chloroquinolines may be considered as follows: for totally symmetric bands including the 00 band, the coupling mechanism should include that in quinoline

$$^1n\pi^* \overset{SO}{\leftrightsquigarrow} {}^3\pi\pi^*$$

and

$$^1(\sigma\pi^*, \pi\sigma^*) \overset{SO}{\leftrightsquigarrow} {}^3\pi\pi^*$$

due to the internal heavy atoms (SO — spin-orbit interaction). We also should consider the second order contributions



which involve the vibronic coupling (V) in the singlet and triplet manifolds, and

$$^1\pi\pi^* \xleftrightarrow{\;V\;} {}^1(\sigma\pi^*, \pi\sigma^*) \xleftrightarrow{\;SO\;} {}^3\pi\pi^*$$

the vibronic coupling in the singlet manifold due to the out-of-plane C-Cl bending vibrations (we assume that due to the energy difference between the $\sigma\pi^*$, $\pi\sigma^*$ states and the T_1 state, the vibronic coupling in the triplet manifold may be neglected [18]).

The phosphorescence spectra of the chloroquinolines show distinct bands in a range about 500 cm^{-1} below the 00 transition. In this range we should expect the presence of an analogue of totally symmetric vibration ~512 in naphthalene, (529 cm^{-1} in quinoxaline) and the out-of-plane skeletal vibrations. The significant contributions of these out-of--plane vibrations to the phosphorescence spectra are characteristic for relatively small azaaromatic molecules [6–10]. Our phosphorescence spectra show the presence of the bands in the range of 450–500 cm^{-1} below the 00 transition. The structures of the phosphorescence spectra in these ranges are sensitive to the position of the Cl atom in the quinoline molecule. The phosphorescence spectra of the chloroquinolines presented in Figs 2 and 3 show that the importance of different out-of-plane vibrations is dependent on the position and number of the chlorine atoms substituted in the quinoline molecule. The substitution of the chlorine atom increases the activity of the out-of-plane skeletal vibrations apart from the appearance of the vibronic bands connected with the C-Cl bending.

Deactivation of the excited states of the chloroquinolines

a. Deactivation of the S_1 state

The energies of the lowest singlet state show a small dependence on the position of the chlorine atom for mono-substituted quinolines. The vibrational structure of absorption and the fluorescence spectra of the chloroquinolines in ethanol suggest that the lowest singlets are of the $\pi\pi^*$ type. The radiative lifetimes estimated from the intensity of the first absorption bands of the chloroquinolines are in the range of 60–80 ns. However, the fluorescence quantum yields of the chloroquinolines are very dependent on the position of the chlorine atom and the solvent used. In ethanol at 77 K all chloroquinolines studied show the fluorescence, whereas in the hydrocarbon solvents we only found the fluorescence emission for 2-ClQ and 2,4-DClQ. The measurements of the intersystem crossing yields for quinoline itself [24] show the significant contribution of the $S_1 \rightarrow S_0$ internal conversion to the deactivation of S_1 state. Methyl derivatives of quinoline in hexane at 77 K show negligible fluorescence $\Phi_{FS}/\Phi_{PT} < 0.01$, whereas in ethanol they have remarkable fluorescence intensity $\Phi_{SF}/\Phi_{PT} \geqslant 0.8$ [23]. The substitution of the chlorine atom into the quinoline molecule results in approximately a 10-fold decrease in the Φ_{SF}/Φ_{PT} ratio relative to that in methylquinolines. The changes involve both acceleration of the $S_1 \rightarrow T$ intersystem crossing and the decay of the triplet state for the chloroquinolines. The decays of the singlet S_1 states of the chloroquinolines indicate the interstate $^1n\pi$ and $^1\pi\pi^*$ interactions. The promotion of the fluorescence emission for 2-ClQ and 2,4-DClQ and relatively small influence of the chlorine atom in position 2 on the phosphorescence lifetimes suggest a remarkable blue shift in the $^1n\pi$ electronic state for 2-ClQ and 2,4-DClQ larger than for the other chloroquinolines.

b. Deactivation of the triplet state

The phosphorescence quantum yields of the chloroquinolines are of the same order of magnitude as for quinoline [22]. The phosphorescence quantum yield for 2-ClQ in ethanol at 95 K is equal to 0.35. Simultaneously, 2-ClQ have the longest phosphorescence lifetimes as compared with other mono-chloro-quinolines. Thus, the chlorine atom in position 2 decreases the rate constant of $T_1 \rightarrow S_0$ intersystem crossing. The phosphorescence lifetime of 2-ClQ is more than two times longer than for the monochloronaphthalenes (1-$ClC_{10}H_7$–0.33 s, 2-$ClC_{10}H_7$–0.38 s [15]). Similarly, the phosphorescence lifetime of 2,4-DClQ is comparable with that of monochloronaphthalenes. The triplet lifetimes of the chloroquinolines show a regular dependence on the distance between the nitrogen atom and the chlorine atom. The shortest triplet lifetime shows 6-ClQ, where the decay constant is approximately the sum of the contributions connected with the nitrogen atom (as in quinoline) and the chlorine atom (as for an internal heavy atom effect in the chloronaphthalenes). The position dependence clearly demonstrates the competition between $^1n\pi$, $^3\pi\pi^*$ and $^3\pi\pi^* \rightsquigarrow {}^1\sigma\pi^*/\pi\sigma^*$ coupling routes in chloroquinolines. A similar behaviour was found for 2,4-dichloroquinoline, where the triplet lifetime is longer than for 4-chloroquinoline. The dependence of the triplet lifetimes on the solvent polarity shows the importance of the $n\pi^* \leftrightsquigarrow \pi\pi^*$ spin-orbit coupling for the triplet decay of the chloroquinolines.

In Table III the phosphorescence lifetimes of the chloroquinolines in the CCl_4 matrix are also presented. These lifetimes are shorter than those in ethanol and hydrocarbon solvents. Simultaneously, the phosphorescence intensity of the chloroquinolines in the CCl_4 matrix is smaller than in other solvents. In the CCl_4 matrix there is a substantial acceleration of the non-radiative transitions for the chloroquinolines. We cannot treat the CCl_4 matrix as a typical heavy atom matrix. Probably a complex formation between an aromatic molecule and CCl_4 influences the non-radiative relaxation of the singlet and triplet states.

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