QUASILINEAR PHOSPHORESCENCE SPECTRA OF 2-, 4-, 6-, 7- AND 8-METHYLQUINOLINE IN CRYSTALLINE n-PARAFFINS AT 77°K

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Phosphorescence spectra ($T \rightarrow S_0$ transition) of 2-, 4-, 6-, 7- and 8-methylquinoline in ethyl alcohol, methylcyclohexane and n-paraffins have been examined at 77°K. In n-paraffins, particularly in n-pentane and n-hexane, spectra show quasilinear structure with different multiplicity. The spectra have similar structure. Vibrational analyses of molecules in the ground singlet state (S_0) have been performed. Internal vibrations in molecules found in quasilinear phosphorescence spectra are in agreement with those found in Raman and infra-red spectra. The quasilinear phosphorescence spectra of methylquinoline have been compared with those of quinoline. The influence of solvent on the structure and position of spectra have also been discussed.

The green phosphorescence spectra of five methyl-substituted quinolines, namely, 2-, 4-, 6-, 7- and 8-methylquinoline, have been investigated earlier [1, 2]. Phosphorescence spectra of these molecules are rather similar to the phosphorescence spectrum of quinoline; they occur approximately in the region 4550–5900 Å and in each molecule they consist of 10–15 vibronic bands. The lifetime of phosphorescence in various molecules depends on temperature and solvent, and amounts from 0.5–3 sec. Methylquinolines are completely non-fluorescent in non-polar solvents such as n-paraffins, benzene, methylcyclohexane, isopentane, cyclohexane whereas they are fairly well fluorescent in alcohols which are capable of making hydrogen bond with nitrogen atoms. In methyl-substituted quinolines, as in the case of quinoline [3, 4, 5] and other N-heterocycles [3, 6, 7, 8], the lowest singlet and triplet states are (π, π^*) or (n, π^*). As phosphorescence of N-heterocycles exhibits properties resembling those of the phosphorescence of the corresponding hydrocarbons, it is plausible to infer that the lowest triplet state is the $^3(\pi, \pi^*)$ state and that phosphorescence emission occurs in transition from the $^3(\pi, \pi^*)$ state to the ground state (S_0).

The absence of fluorescence in non-polar solvent is caused by increased spin-orbital interaction, which is the result of the influence of n-electrons. The increase in the internal conversion to the phosphorescence level decreases the fluorescence yield, increases the phosphorescence yield, and can cause the complete quenching of fluorescence.

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TABLE I (continued)

Intensity	Wavelength	Wavenumber	Multiplet $\Delta\tilde{\nu}$	$\Delta\tilde{\nu}$	Analysis
10	4676.9	21382			$0 - 0'$
10	4688.0	21331	51		$0_1 - 0'_1$
2	4737.0	21110	272		$0_2 - 0'_2$
4	4794.5	20857		525	$0 - 525$
4	4804.5	20814	43	517	$0_1 - 517$
0	4856.0	20593	264	517	$0_2 - 517$
9	5001.8	19993		1389	$0 - 1389$
9	5051.0	19798		1584	$0 - 1584$
4	5190.0	19268		2114	$0 - 2114 \cong 1584 + 525$
7	5376.1	18601		2781	$0 - 2781 \cong 2 \cdot 1389$
9	5430.2	18416		2966	$0 - 2966 \cong 1584 + 1389$
7	5491.5	18210		3172	$0 - 3172 \cong 2 \cdot 1584$
5	5589.5	17891		3491	$0 - 3491 \cong 1584 + 1389 + 525$
1	5803.0	17232		4150	$0 - 4150 \cong 3 \cdot 1389$
4	5878.2	17012		4370	$0 - 4370 \cong 2 \cdot 1389 + 1584$
6	5953.3	16797		4585	$0 - 4585 \cong 3 \cdot 1389 + 525$

8-methylquinoline in n-hexane at 77°K, triplet structure

The infra-red spectra of all these methylquinolines have been investigated earlier [9, 10, 11], while the Raman spectra of only 2- and 4-methylquinoline have been reported in the literature [12, 13].

Quasilinear phosphorescence spectra in some N-heterocycles, such as quinoline [14, 15, 16], benzoquinoline [14, 16, 17], dibenzoquinoline [7, 8], obtained at low temperatures have been studied by Shpolskii's method [18] earlier. In this paper the quasilinear phosphorescence spectra of the above-mentioned methylquinolines have been discussed.

1. Experimental

The examined compounds were supplied by BDH, and they were farther purified by distillation. The solvents used were fairly pure, which was controlled by parasitic lumines-cence. The concentration of the frozen solutions was 10^{-3}–10^{-2} mole/litre. The sample in a round quartz cuvette whose diameter was about 1 mm, was cooled rapidly to 77°K with liquid N_2 in a quartz dewar. Excitation at wavelengths shorter than 2900 Å was via a high-pressure mercury lamp Q 400 and interference-reflection filter UV-R-250. The spectra were detected photographically on Kodak R-60 film, by means of a Officine Gali-leo 061 spectrograph. Exposures, with slit width in the range 20–30 μ, were of the order of 15 minutes. The phosphoroscope was not used, as in n-paraffins and methylcyclohexane solutions fluorescence does not occur, whereas in ethyl alcohol it is completely separated from phosphorescence.
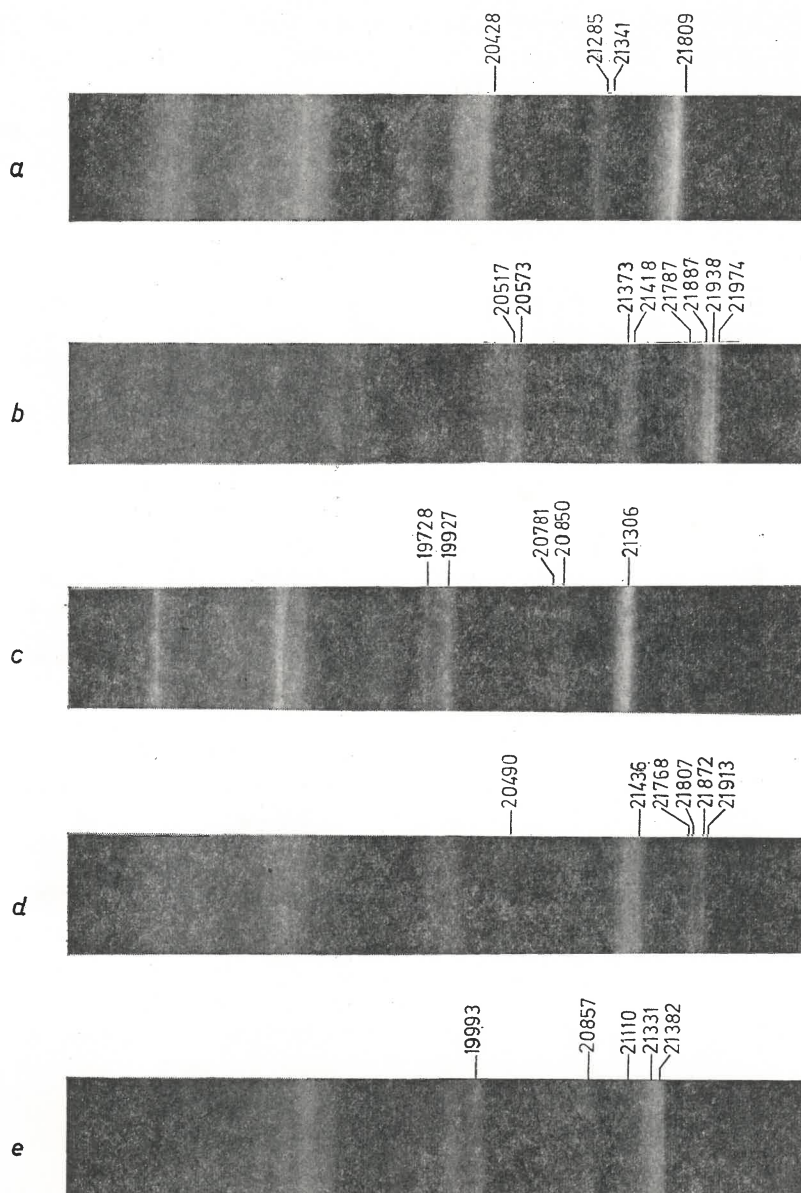
Fig. 1. Phosphorescence spectra of: a) 2-methylquinoline in *n*-hexane, b) 4-methylquinoline in *n*-pentane, c) 6-methylquinoline in *n*-hexane, d) 7-methylquinoline in *n*-pentane and e) 8-methylquinoline in *n*-hexane

2. Results

Experimental results concerning quasilinear phosphorescence spectra of 2-, 4-, 6-, 7- and 8-methylquinoline are qiven in Table I, and the best spectrograms of the spectra obtained are shown in Fig. 1.

2-methylquinoline in *n*-hexane (Fig. 1a) has singlet quasilinear structure. The quasi-lines are against the background of comparatively intense bands about 100 cm⁻¹ wide. The line corresponding to the 0,0 transition is very intense.

4-methylquinoline spectra in *n*-pentane solution (Fig. 1b) show typical quasilinear structure of quartet character. The lines are not accompanied by bands of significant
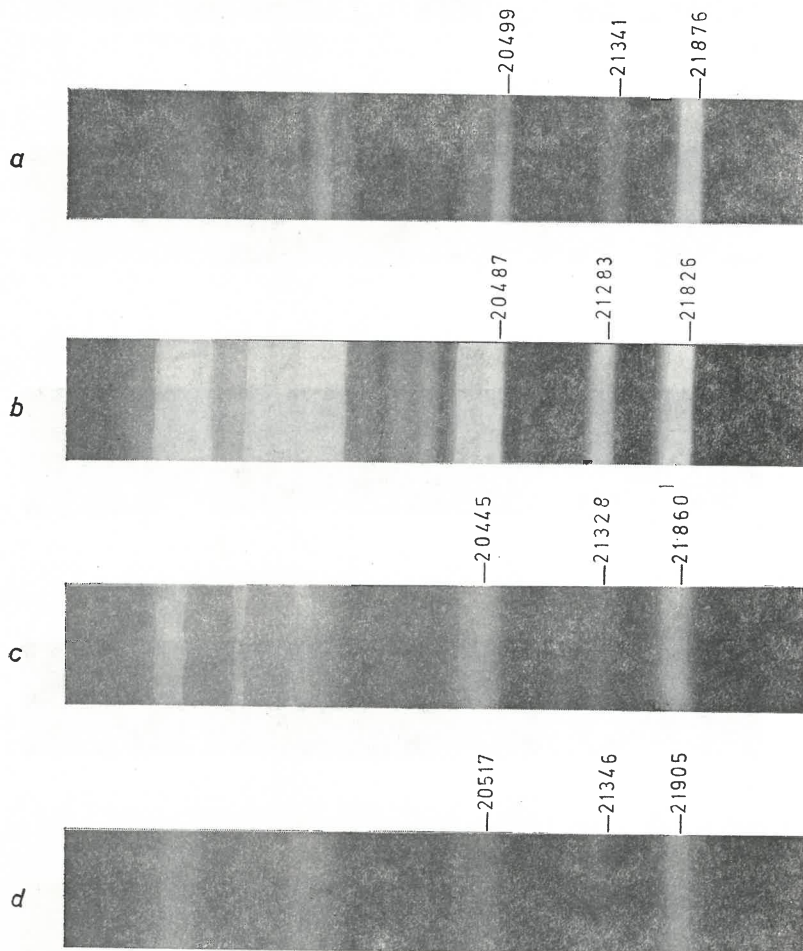

Fig. 2. Phosphorescence spectra of 4-methylquinoline in: a) *n*-hexane, b) *n*-pentane, c) methylcyclohexane and d) ethyl alcohol

intensity. The quartet of 0,0 transition, which is at the same time the most intense in the spectrum, is particularly clear. The lines are about 10 cm⁻¹ wide. Fig. 2 shows the spectrograms of 4-methylquinoline phosphorescence spectrum in four different solvents: *n*-hexane, *n*-heptane, methylcyclohexane and ethyl alcohol. The spectrum in ethyl alcohol and methylcyclohexane shows typical band structure, whereas in *n*-heptane, and particularly in *n*-hexane, quasilinear structure already begins to appear. Thus the solvent effect causes

the wave shift of the spectrum. This is clearly seen in the 0,0 transition, whose wave number in *n*-pentane, *n*-hexane, *n*-heptane, methylcyclohexane, and ethyl alcohol is 21976, 21876, 21826, 21860, 21905 cm^{-1} respectively. It is characteristic that vibronic bands are rather narrow ($\sim$150 cm^{-1}) and separated even in such solvents, as ethyl alcohol and methyl-cyclohexane, in which quasilinear structure in phosphorescence spectrum does not occur.

6-methylquinoline in *n*-hexane (Fig. 1c) shows singlet quasilinear structure. The lines are about 15 cm^{-1} wide and are accompanied by intense bands about 100 cm^{-1}

TABLE II

(Wavenumbers in cm^{-1})

Molecule	Phosphorescence (Present work)	Raman bands[a]	Infra-red bands in chloroform[b]
2-methylquinoline	468	455	
	524	522	
	830		822
	984		970
	1146		1141
	1381	1372	1380
	1569		1570
4-methylquinoline	518	565	
	831		849
	1362	1361	1361
	1566		1573
6-methylquinoline	456		
	525		
	1028		1033
	1379		1376
	1578		1575
7-methylquinoline	482		
	521		
	1026		1034
	1387		1385
	1580		1570
8-methylquinoline	520		
	1386		1383
	1584		1579

[a] M. A. Shashidhar, K. Suryanarayana Rao, *Indian J. Phys.*, **41**, 299 (1967).
[b] A. R. Katritzky, R. Alan Jones, *J. Chem. Soc.*, 2942 (1960).

wide, especially in the 0,0 transition. Besides, in the long-wave region of the spectra an intense background appears.

7-methylquinoline in *n*-pentane (Fig. 1d) presents quasilinear spectrum with quartet structure, at least with regard to the 0,0 transition. The 0,0 transitions shows little intensity when compared to other transitions and has the most typical quasilinear character. In

other vibronic transition multiplicity ranging from triplet to singlet has been identified. The 0,1 transition shows particularly great intensity. The lines are on bands without clear edges and in the long-wave region of the spectrum a very intense background appears.

8-methylquinoline in *n*-hexane solution (Fig. 1e) shows triplet quasilinear structure with lines on intense bands of the same width (~ 100 cm^{-1}) with fairly clearly defined edges. The intensity of the lines, except in the 0,0 transition, is only slightly greater than that of the bands on which they are situated.

Internal vibronic frequencies in molecules of methylquinoline found in quasilinear spectra in this paper (Table II) are slightly different from vibronic frequencies in quinoline found also in quasilinear spectra [14]. The following frequencies were found in quinoline: 524, 805, 1151, 1384 and 1580 cm^{-1}, while in 2-methylquinoline they were: 524, 830, 1146, 1381 and 1569 cm^{-1}, respectively. Besides, these frequencies are in agreement with those found in Raman and infra-red spectra (Table II). The cause of the multiplet splitting of quali-lines could not be ascertained with certainty. Its possible cause is multiplet splitting of electronic ground state in molecules, to which conclusion point some facts which are now under examination.

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