ELECTRONIC SPECTRA AND LUMINESCENCE PROPERTIES OF 4,10-DIAZACHRYSENE IN CRYSTALLINE AND GLASSY MATRICES AT 77 K*, **

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Highly resolved absorption, fluorescence and phosphorescence spectra of 4,10-diazachrysene (4,10-DACH) in Shpolskii matrices were obtained, at 77 K. The vibrational analysis of these spectra, as well as the examination of the Raman spectrum of 4,10-DACH showed only totally symmetric (a_g) fundamental vibrations in the electronic spectra of 4,10-DACH. The energies of the $S_1(\pi,\pi^*)B_u$, $S_2(\pi,\pi^*)B_u$ and $T_1(\pi,\pi^*)B_u$ electronic states of the 4,10-DACH molecule are very close to the energies of the respective states of the chrysene molecule. The phosphorescence lifetime of 4,10-DACH in hydrocarbon matrices is 1.03 ± 0.02 s. The major mechanism responsible for phosphorescence seems to be a direct spin-orbit coupling of the T_1 state with the lowest $^1(n,\pi^*)A_u$ state, which is slightly above the $S_2(\pi,\pi^*)$ state. The lowest $^3(n,\pi^*)$ state is most probably above the $S_1(\pi,\pi^*)$ one. The experimental results were compared with the results of calculations of the electronic structure of the 4,10-DACH molecule in the PPP CI approximation.

1. Introduction

The electronic spectra and luminescence properties of chrysene were the subject of numerous investigations. Highly resolved absorption and luminescence spectra of chrysene were also obtained in Shpolskii matrices [1–3]. However, very little is known so far about the electronic spectra and luminescence properties of azachrysenes.

This paper presents the results of investigations into highly resolved UV-absorption and luminescence spectra of frozen solutions of 4,10-DACH (compare the formula in Fig. 1). The UV-absorption spectra of liquid solutions of this compound in alcohols have been described by several authors [4–6], however the results given in [4] and [5] seem to be

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doubtful in the light of more recent research [6] A thorough examination of the lowest triplet state of the 4,10-DACH molecules was carried out by Bulska et al. [7, 8], who first obtained the phosphorescence and *T–T* absorption spectra of 4,10-DACH. No published data concerning the fluorescence of 4,10-DACH are known to us.

2. Experimental

4,10-DACH purified by sublimation was used for the experiments. Hydrocarbon solvents were purified by column chromatography and dried over metallic sodium. Alcohol solvent were distilled and checked for purity in a manner similar to that described in [9].

The luminescence and absorption spectra of 4,10-DACH solutions ($c = 10^{-3} - 10^{-5}$ M), frozen at 77K, were obtained by the photographic method using a grating spectrograph STE-1 (absorption and fluorescence spectra), a quartz spectrograph ISP-22 (absorption spectra) and triprismatic glass spectrograph (C. Zeiss, Jena) with an $F = 700$ mm camera (phosphorescence spectra). The method of freezing the solutions and the manner of exciting the spectra were similar to those in [10]. Other experimental details have been described in [11].

The Raman spectra of 4,10-DACH were registered with the use of a JEOL S1 spectrometer equipped with an argon laser ($\lambda = 5148$ Å and 4880 Å). The degree of depolarization ϱ of the Raman bands ($0 \leqslant \varrho \leqslant 0.75$) was measured.

The phosphorescence decay curves of 4,10-DACH in the frozen solutions were registered on photorecording paper with the use a loop oscillograph N-115 (made in USSR). Previous to measurements the alcohol solutions were degassed. In the case of exponential decays, observed with solutions of sufficiently low concentrations (see Part 5), the best value of τ_{ph} was calculated numerically with the use of an EMC "ODRA 1204". Each value was approximated on the basis of the analysis of twenty decay curves.

3. Absorption spectra

We have examined the structure of the absorption spectra in the region of 3600–3000 Å which, according to [6], involves two electronic transitions (α- and p-bands).

In n-hexane, n-heptane and partly in n-octane matrices the spectra showed a quasi-linear multiplet structure (Fig. 1), characteristic of the Shpolskii spectra [12]. In the range of concentrations 10^{-3}–10^{-5} M the width of the lines slightly decreases along with decreasing concentrations of the solutions.

The spectra of the first electronic transition in each matrix begin with a group of strong lines showing resonance agreement (within the accuracy of measurement) with the initial group of 4,10-DACH fluorescence spectra lines in an identical matrix (cf. Table I, columns 1 and 2). So these groups represent the multiplets of 0–0 transition of 4,10-DACH molecules occupying different sites of the crystalline lattices of the matrices [12]. The values shown in Table I are very similar to the $\tilde{\nu}_{00}$ value of the $S_1 \leftarrow S_0$ transition of a chrysene molecule, although the multiplicities of the spectra of both compounds are different [3].

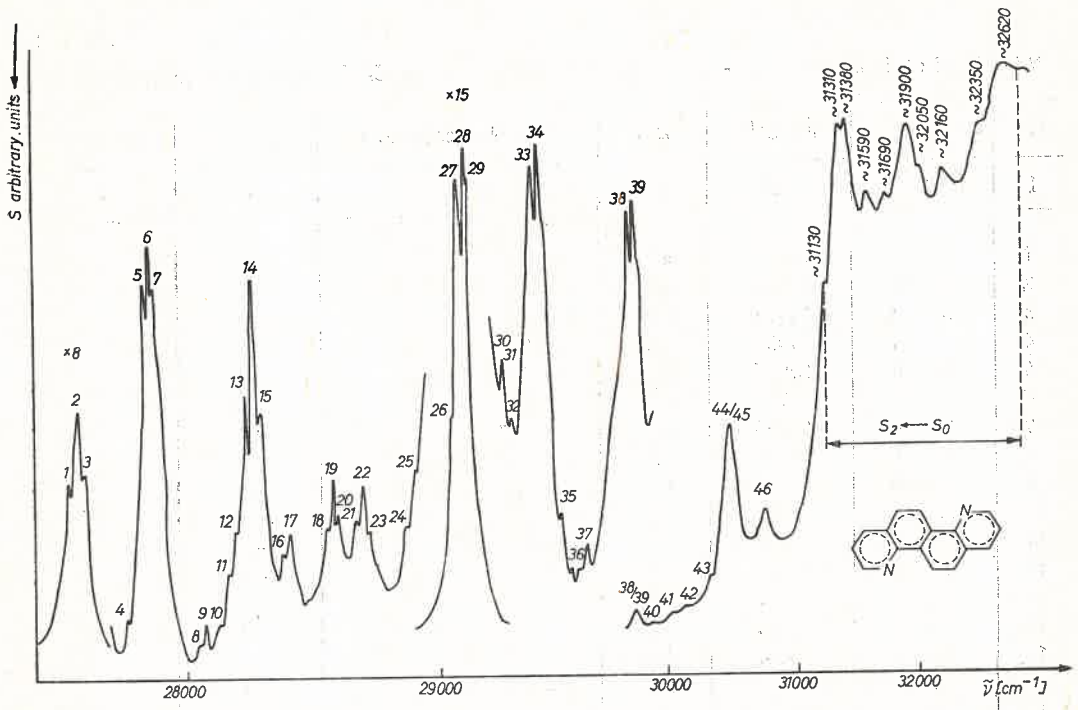

Fig. 1. Microphotometer curves (redrawn) of the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ absorption spectra of 4,10-DACH in the n-heptane matrix, at 77 K. The vibronic lines of the $S_1 \leftarrow S_0$ transition are numbered according to Table II. Wave numbers of band peaks in the range of the $S_2 \leftarrow S_0$ transition are given

TABLE I

Multiplets of the 0–0 transitions in the electronic spectra of a 4,10-DACH molecule in various hydrocarbon matrices, at 77 K ($\tilde{\nu}_{00}$ in cm^{-1})

Matrix	Transition		
	$S_1 \leftarrow S_0$	$S_1 \rightarrow S_0$	$T_1 \rightarrow S_0$
n-hexane	27764	27762	20456
	27737	27736	20407
	27718	27717	20356
	27674	27672	20335
	not detectable line	27645	20256
	27592	27593	20218
n-heptane	27705	27707	20317
	27682	27681	20282
	27652	27653	
n-octane	27659	27657	20316
	27623	27620	20291
	27599	27595	20263
			20222

TABLE II

Vibrational analysis of the $S_1 \leftarrow S_0$ absorption system of 4,10-DACH in n-heptane matrix, at 77 K

No	λ (Å)	$\tilde{\nu}$ (cm^{-1})	Int.	Possible assignment	$\Delta\tilde{\nu}_{calc} - \Delta\tilde{\nu}_{obs}$	Remarks
1	2	3*	4**	5	6	7
1	3615.3	27653	s	$(0-0)_1$		
2	3611.3	27683	vs	$(0-0)_2$		
3	3608.2	27707	ms	$(0-0)_3$		
4	3578.3	27938	mw	0_1-285	-1	
5	3574.8	27966	s	0_2-285	$+2$	
6	3571.4	27992	s	0_3-285	0	
7	3554.6	28124	w	0_1-472	$+1$	
8	3551.1	28152	m	0_2-472	$+3$	
9	3547.1	28184	vw	0_3-472	-5	
10	3542.1	28224	mw	$0_1-285\times2$	-1	
11	3539.0	28249	m	$0_2-285\times2$	$+4$	
12	3532.9	28297	ms	0_1-645	$+1$	
13	3529.2	28327	vs	0_2-645	-1	
14	3526.0	28353	mw	0_3-645	0	
15	3517.1	28424	mw	0_1-771	0	
16	3513.4	28454	m	0_2—771	0	
17	3497.6	28584	w	$0_1-285-645$	-1	
18	3494.2	28611	ms	$0_2-285-645$	$+2$	
19	3491.5	28633	w	$0_3-285-645$	$+4$	
20	3483.9	28695	m	0_1-1038	-4	
21	3480.8	28721	ms	0_2-1038	0	
22	3478.1	28743	w	0_3-1038	$+2$	
23	3460.4	28890	mw	$0_1-472-771$	$+6$	diffuse
24	3456.5	28923	mw	$0_2-472-771$	$+3$	diffuse
25	3441.7	29048	m	0_1-1392	-3	
26	3438.7	29072	vvs	0_1-1418 and	-1	
				0_2-1392	$+3$	
27	3435.5	29099	vvs	0_2-1418 and	$+2$	
				0_3-1392	0	
28	3432.4	29126	w	0_3-1418	-1	strong
29	3424.6	29192	w	$0_1-771\times2$	$+3$	background
30	3421.4	29219	w	$0_2-771\times2$ and	$+6$	
				0_1-1568	$+2$	
31	3417.5	29253	m	0_2-1568	-2	
32	3405.4	29357	vs	$0_1-285-1418$ and	-1	
				$0_2-285-1392$	$+3$	
33	3402.2	29384	vs	$0_2-285-1418$ and	$+2$	
				$0_3-285-1392$	0	
34	3384.5	29538	mw	$0_1-472-1418$ and	$+5$	
				$0_2-472-1392$	$+9$	
35	3380.7	29571	m	$0_2-472-1418$ and	$+2$	
				$0_3-472-1392$	0	
36	3367.3	29689	ms	$0_1-645-1392$	$+1$	

TABLE II (cont.)

1	2	3*	4**	5	6	7
37	3363.7	29721	s	$0_2-645-1392$ and	−1	
				$0_1-645-1418$	−5	
38	3361.1	29744	s	$0_3-645-1392$ and	0	
				$0_2-645-1418$	+2	
39	3345.9	29878	m	$0_2-771-1418$	−6	
40	3330.4	30017	ms	$0_2-285-645-1418$	+14	
41	3319.2	30119	ms	$0_2-1038-1392$	−6	
42	3297.8	30310	m	$0_{1,2}-472-771-1418$	−19	diffuse
43	3278.7	30492	s	$0_1-1418\times2$ or/and	−3	
				$0_2-1392-1418$	+1	
44	3275.9	30517	s	$0_2-1418\times2$ or/and	+2	
				$0_3-1392-1418$	0	
45	3247.9	30781	m	$0_2-285-1392-1418$	+7	

* reduced to vacuum, ** s — strong, m — medium, w — weak, v — very.

Since the sextet structure of the spectrum examined in an n-hexane matrix considerably complicates its analysis, we carried out a vibrational analysis of the spectrum obtained in an n-heptane matrix (Table II). The analysis resulted in distinguishing eight fundamental vibration frequencies of the 4,10-DACH molecule in the S_1 state. Among them the most active appeared the 285, 645, 1392 and 1418 cm^{-1} vibrations, participating in different combinations. The lines of vibronic transitions with participation of the fundamentals 1392 and 1418 cm^{-1} belong to the most intensive in the spectrum. Most of the identified fundamental vibration frequencies, appearing in the spectrum of $S_1 \leftarrow S_0$ transition of 4,10-DACH molecules, have values similar to the fundamentals of chrysene molecules in S_1 state [2, 3].

Beginning from about 3350 Å the lines of vibronic transitions, belonging to the first absorption system, are distinctly broadened (see Table II), probably due to the close proximity of the $S_2 \leftarrow S_0$ electronic transition. We ascribe its origin to the band 3210 Å (31130 cm^{-1}, see Fig. 1), which is in a satisfactory agreement with the data given by Nekrasov et al. [6]. In the region of the second electronic transition the examined spectrum loses its quasilinear structure.

In frozen alcohol glasses (ethanol, n-butanol-1) the absorption spectrum of 4,10-DACH is composed of wide bands (halfwidths of the order 100 cm^{-1} — Fig. 2a) already in the region of the $S_1 \leftarrow S_0$ transition. The maximum of the first band corresponds to the wave number 27540 cm^{-1}, while the band with the peak of about 31270 cm^{-1} corresponds to the beginning of $S_2 \leftarrow S_0$ transition. Slight shifts of the spectra of both transitions in hydroxylic matrices, in respect to the spectra obtained in hydrocarbon matrices, indicate the π, π^* type of S_1 and S_2 excited states of the 4,10-DACH molecule.

Quite an interesting structure is shown by the absorption spectra of 4,10-DACH in microcrystalline matrices, such as formed by n-heptanol-1 and n-octanol-1 after freezing (Fig. 2*b*). In these spectra there appear quasilines, alongside a few broader bands. The

$S_1 \leftarrow S_0$ transition spectrum in n-octanol matrix begins with the quintet 0–0 (27304–27751 cm^{-1}) which, within the limits of measurement accuracy, is in resonance agreement with the 0–0 transition lines of the fluorescence spectrum in the same matrix. The quasi-

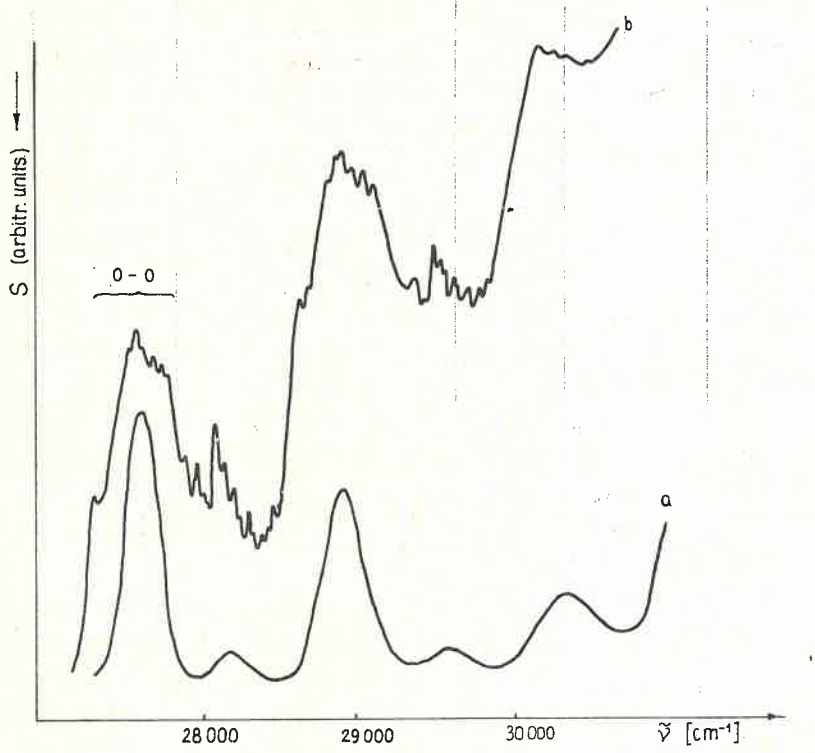

Fig. 2. Microphotometer curves (redrawn) of the $S_1 \leftarrow S_0$ absorption spectra of 4,10-DACH (*a*) — in n-butanol-1 glass (*b*) — in a microcrystalline n-octanol-1 matrix, at 77 K

linear structure of the spectra of some aromatic hydrocarbons in matrices formed by higher aliphatic alcohols was pointed out already in Shpolskii's early papers [12], though in later experiments such matrices were rather not used.

4. Fluorescence spectra

The $S_1 \rightarrow S_0$ emission spectrum of 4,10-DACH molecules extends in the range from about 3600 Å to 4100 Å. The highly resolved vibronic structure of this spectrum was obtained in the same hydrocarbon matrices in which the spectrum of the first absorption system showed a quasilinear structure. Fig. 3 shows the microphotometric curve of 4,10-DACH fluorescence spectrum in an n-heptane matrix. The lines of 0–0 multiplets (cf. Table I) in the examined spectra are very intensive. In the range 10^{-3}–10^{-5} M no visible effect of concentration on the structure of the spectra was found.

The vibrational analysis of the 4,10-DACH fluorescence spectrum in frozen n-heptane is shown in Table III. In this spectrum 10 fundamental vibration frequencies of the

molecule in the ground state were identified. Among them only the vibrations 483 and 675 have no corresponding frequencies in the fluorescence spectrum of chrysene [3]. In the spectrum predominating are frequencies 293, 1402 and 1433 cm^{-1}. Almost all registered

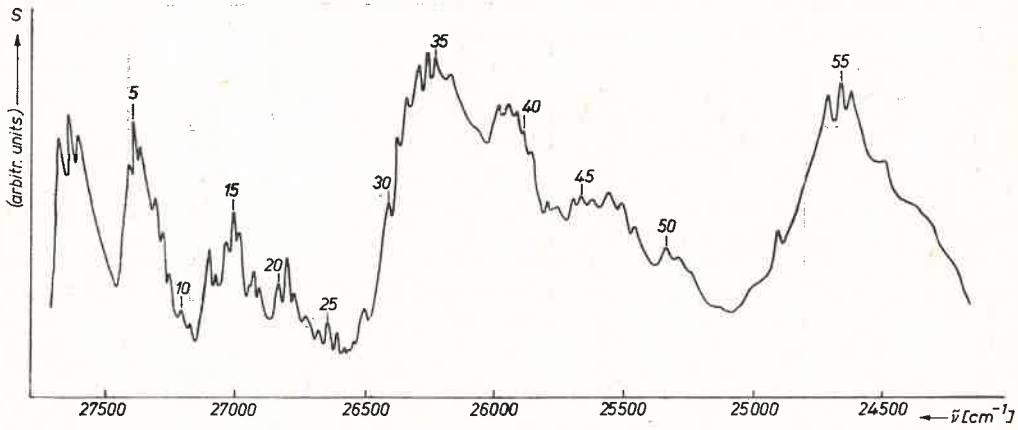

Fig. 3. Microphotometer curve (redrawn) of the fluorescence spectrum of the 4,10-DACH in an n-heptane matrix, at 77 K. The lines are numbered according to Table III

vibronic transitions outside the region of fundamental vibration frequencies are combinations with participation of these vibrations or their overtones (Table III).

The 675 cm^{-1} frequency (see lines 14–16, Table III) has been ascribed to the fundamental vibration of the 4,10-DACH molecule in the S_0 state, though formally this frequency could have been assigned as a combination of fundamental frequencies 293 and 383 cm^{-1}. This interpretation is corroborated as well by a considerable intensity in lines 14–16 in the fluorescence spectrum as the presence of a strong band of about 670 cm^{-1} in the Raman spectrum of 4,10-DACH (see Part 6). Moreover, vibration 645 cm^{-1} in the absorption spectrum of 4,10-DACH, which cannot be interpreted as a combination of two vibrations, seems to correspond to the one at 675 cm^{-1} (cf. Table II).

On the basis of vibrational analyses of quasilinear $S_1 \leftarrow S_0$ and $S_1 \rightarrow S_0$ spectra of the 4,10-DACH molecule it can be stated that the values of most fundamental vibration frequencies are very similar in both spectra, particularly concerning the most active vibrations. Nevertheless, the observed disturbance of mirror-image symmetry of these spectra is most probably caused by vibronic coupling between $S_1(\pi, \pi^*)B_u$ and $S_2(\pi, \pi^*)B_u$ states through totally symmetric vibrations; the energies of these states differ by about 0.4 eV only (cf. Part 6). Similar disturbances of the mirror-image symmetry in the spectra of aromatic hydrocarbons, chrysene among others, were thoroughly analyzed by Bolotnikova et al. [13].

The fluorescence spectrum of 4,10-DACH in n-butanol glass consists of few featureless bands. To the 0–0 transition corresponds the band with a peak 27390 cm^{-1}, showing a batochromic shift in relation to a corresponding transition in hydrocarbon matrices.

TABLE III

Vibrational analysis of the $S_1 \rightarrow S_0$ fluorescence spectrum of 4,10-DACH in n-heptane matrix, at 77 K

No	λ (Å)	$\tilde{\nu}$ (cm^{-1})	Int.	Possible assignment	$\Delta\tilde{\nu}_{calc} - \Delta\tilde{\nu}_{obs}$	Remarks
1	2	3*	4**	5	6	7
1	3608.3	27706	m	$(0-0)_1$		
2	3611.6	27681	s	$(0-0)_2$		
3	3615.3	27652	ms	$(0-0)_3$		
4	3647.0	27412	mw	0_1-293	−1	
5	3650.3	27387	vs	0_2-293	−1	
6	3653.9	27360	s	0_3-293	+1	
7	3658.4	27326	w	0_1-383	+3	
8	3662.3	27297	mw	0_2-383	−1	
9	3666.5	27266	mw	0_3-383	−3	
10	3675.9	27197	m	0_2-483	−1	diffuse
11	3679.5	27170	m	0_3-483	+1	
12	3688.6	27103	ms	$0_2-293\times2$	+8	
13	3694.0	27063	mw	$0_3-293\times2$	−3	
14	3698.9	27035	w	0_1-675 and	+4	
				$0_1-293-383$	+5	
15	3702.3	27003	vs	0_2-675 and	+3	
				$0_2-293-383$	−2	
16	3706.1	26975	m	0_3-675 and	+2	
				$0_3-293-383$	−1	
17	3711.5	26936	vw	0_1-777 and	+7	diffuse
				$0_1-293-483$?	+6	
18	3716.7	26898	ms	0_2-777 and	−6	
				$0_2-293-483$	−7	
19	3720.2	26872	w	0_3-777 and	−3	
				$0_3-293-483$	−4	
20	3728.1	26815	m	0_1-893 and	+2	
				$0_1-293\times3$	−12	
21	3732.1	26787	ms	0_2-893 and	−1	
				$0_2-293\times3$	−15	
22	3736.1	26759	m	0_3-893 and	0	
				$0_3-293\times3$	−4	
23	3742.7	26711	m	$0_2-293-675$ or	−2	
				$0_2-293\times2-383$	−1	
24	3748.3	26671	mw	0_1-1037	+2	diffuse
25	3752.3	26643	m	0_2-1037	−1	diffuse
26	3756.5	26613	w	0_3-1037	−2	diffuse
27	3769.1	26524	vw	$0_1-293-893$ and/or	+4	
				$0_1-293\times4$	−10	
28	3773.7	26492	mw	$0_2-293-893$ and/or	−3	
				$0_2-293\times4$	−17	
29	3786.1	26405	m	0_1-1298	−3	
30	3789.3	26383	vs	0_2-1298 and	0	
				$0_1-293-1037$	+7	
31	3793.1	26357	ms	0_3-1298 and	+3	
				$0_2-293-1037$	+6	

TABLE III (cont.)

1	2	3*	4**	5	6	7
32	3800.2	26307	mw	0_1-1402	+3	
33	3804.1	26280	vvs	0_2-1402 and	+1	
				0_1-1433	+7	
34	3809.0	26246	vs	0_3-1402 and	−4	
				0_2-1433 and	−2	
				$0_1-293\times5$	+5	
35	3813.6	26214	ms	$0_1-293\times2-893$ and/or	−13	
				0_3-1433 and	−5	
				$0_2-293\times5$	−2	
36	3819.6	26173	m	$0_2-483-1037$ and	+12	
				$0_3-293\times5$	−14	
37	3846.8	25988	s	$0_2-293-1402$ and	+2	
				$0_1-293-1433$	+8	
38	3852.1	25952	s	$0_3-293-1402$ and	−5	
				$0_2-293-1433$ and	−3	
				$0_1-293\times6$	+4	
39	3856.5	25923	m	$0_1-383-1402$ and	+2	
				$0_3-293-1433$ and	−3	
				$0_2-293\times6$	0	
40	3859.6	25902	w	$0_2-383-1402$ and	+6	
				$0_3-293\times6$	+8	
41	3862.7	25881	w	$0_3-383-1402$	+14	
42	3866.3	25857	w	$0_2-383-1433$	−8	diffuse
43	3877.8	25780	vw	$0_2-483-1433$	+15	diffuse
44	3888.3	25711	m	$0_2-675-1298$	+3	diffuse
45	3890.5	25697	m	$0_2-293\times2-1402$	+4	diffuse
46	3894.0	25673	m	$0_3-293\times2-1402$	+9	diffuse
47	3904.5	25604	m	$0_1-675-1433$ and	+6	
				$0_2-675-1402$	0	
48	3908.1	25581	m	$0_2-675-1433$ and	+8	
				$0_3-675-1402$	+6	
49	3910.6	25564	vw	$0_3-675-1433$ or	+20	
				$0_2-293-383-1433$	−9	
50	3937.6	25389	vw	$0_1-893-1433$ or	+9	
				$0_2-893-1402$	+3	
51	3942.3	25359	vw	$0_2-893-1433$ and	+4	
				$0_3-893-1402$	+2	
52	3947.9	25323	mw	$0_3-893-1433$ and	−3	
				$0_2-293-675-1402$	+11	
53	4017.4	24885	mw	$0_1-1402-1433$ and/or	+14	
				$0_2-1402\times2$	+8	
54	4022.8	24851	vs	$0_2-1402-1433$ and/or	+5	
				$0_3-1402\times2$	+3	
55	4028.7	24815	ms	$0_3-1402-1433$ and/or	−2	
				$0_2-1433\times2$	0	
56	4078.4	24513	ms	$0_2-293-1433\times2$	−9	

* reduced to vacuum, ** s — strong, m — medium, w — weak, v — very.

The Stokes shift of this band relative to the first band of the absorption spectrum in the same glassy matrix is about 150 cm^{-1}.

The short-wave part of the 4,10-DACH fluorescence spectrum in microcrystalline matrices formed by higher aliphatic alcohols shows a quasilinear structure (cf. Part 3).

5. Phosphorescence

Frozen solutions of 4,10-DACH show green phosphorescence, extending within the spectral range from about 4900 to 6000 Å (compare [7, 8]). Like in the case of absorption and fluorescence spectra, quasilinear phosphorescence spectra with multiplet structure were obtained in n-hexane, n-heptane and n-octane matrices (cf. Table I).

Figure 4 shows the phosphorescence spectrum of 4,10-DACH in frozen n-heptane and Table IV — the results of vibrational analysis of this spectrum. From among eleven

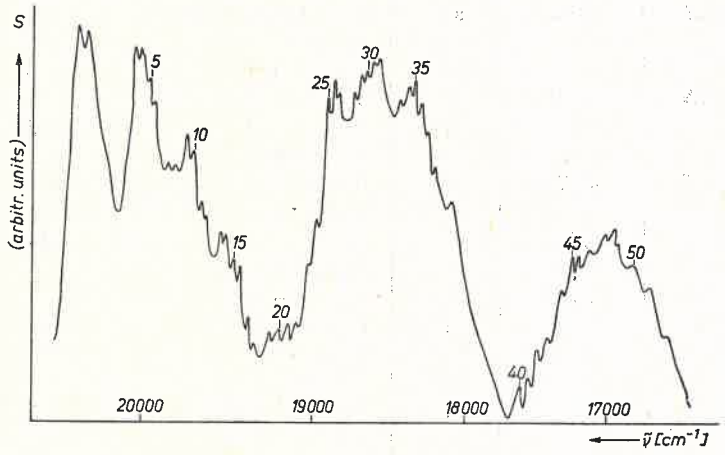

Fig. 4. Microphotometer curve (redrawn) of the phosphorescence spectrum of 4,10-DACH in n-heptane matrix, at 77 K. The lines are numbered according to Table IV

identified fundamental vibration frequencies the most active in the spectrum of $T_1 \rightarrow S_0$ transition are 292, 1398 and 1434 cm^{-1} fundamentals forming the overtones and numerous combinations. These are, within the limits of measurement accuracy (± 5 cm^{-1}), the same fundamentals which are the most active in the fluorescence spectrum of 4,10-DACH (compare above).

We have observed a close similarity of the structure of quasilinear phosphorescence spectra of 4,10-DACH and chrysene [3], although the multiplicities of the spectra of these compounds in identical crystalline matrices are different. The fundamental vibration frequencies found in the spectra of both compounds are very similar. The same frequencies are most active in the phosphorescence spectra of 4,10-DACH and chrysene.

The phosphorescence spectrum of 4,10-DACH in n-hexanol glass consist of nine bands. The first strong band with a peak 20145 cm^{-1} corresponds to the 0–0 transition

TABLE IV

Vibrational analysis of the $T_1 \rightarrow S_0$ phosphorescence spectrum of 4,10-DACH in n-heptane matrix, at 77 K

No	λ (Å)	$\tilde{\nu}$ (cm^{-1})	Int.	Possible assignment	$\Delta\tilde{\nu}_{calc} - \Delta\tilde{\nu}_{obs}$	Remarks
1	2	3*	4**	5	6	7
1	4920.6	20317	vs	$(0-0)_1$		
2	4929.1	20282	s	$(0-0)_2$		diffuse
3	4992.3	20025	vs	0_1-292	0	
4	5000.8	19991	s	0_2-292	+1	diffuse
5	5015.9	19931	mw	0_1-389	+3	background
6	5026.5	19889	w	0_2-389	+6	
7	5040.4	19834	m	0_1-481	−2	
8	5048.3	19803	mw	0_2-481	+3	diffuse
9	5066.6	19732	s	$0_1-292\times2$	−1	
10	5075.7	19696	m	$0_2-292\times2$	−2	diffuse
11	5091.2	19636	mw	0_1-679 and/or	−2	
				$0_1-292-389$	0	
12	5099.0	19606	vw	0_2-679 and/or	+3	
				$0_2-292-380$	+5	
13	5115.4	19543	m	0_1-773 and/or	−1	
				$0_1-292-481$	−1	
14	5124.0	19511	mw	0_2-773 and/or	+2	diffuse
				$0_2-292-481$	+2	
15	5141.6	19444	mw	$0_1-292\times3$	+3	
16	5151.7	19406	w	$0_2-292\times3$	0	
17	5167.2	19348	vw	$0_1-292-679$ and /or	+3	
				$0_1-292\times2-389$	+4	
18	5177.5	19309	vw	$0_2-292-679$ and/or	−1	
				$0_2-292\times2-389$	0	
19	5192.0	19255	m	$0_1-292-773$ and/or	+3	
				$0_1-292\times2-481$	+3	
20	5200.4	19224	w	$0_2-292-773$ and/or	+7	
				$0_2-292\times2-481$	+7	
21	5210.9	19185	w	0_1-1132	0	
22	5220.9	19149	w	0_2-1132 and	−1	
				$0_1-292\times4$	0	
23	5257.3	19017	mw	0_1-1300	0	
24	5284.7	18917	s	0_1-1398	−2	
25	5293.4	18886	s	0_2-1398 and	+2	
				0_1-1434	+3	
26	5304.6	18846	mw	0_2-1434 and	−2	strong
				$0_1-292\times5$	−11	background
27	5333.8	18743	m	0_1-1572	−2	
28	5342.8	18712	ms	0_2-1572 and	+2	
				0_1-1599	−6	
29	5349.3	18689	ms	0_2-1599	+6	
30	5368.2	18623	s	$0_1-292-1398$	−4	
31	5378.2	18588	s	$0_2-292-1398$	−4	
32	5417.2	18455	mw	$0_1-292-1572$	+2	

TABLE IV (cont.)

1	2	3*	4**	5	6	7
33	5426.3	18424	mw	$0_2-292-1572$ and/or	+6	
				$0_1-292-1599$	−2	
34	5433.2	18400	ms	$0_1-481-1434$ and	−2	
				$0_2-292-1599$	+9	
35	5442.8	18368	w	$0_2-481-1434$	+1	
36	5452.3	18336	w	$0_1-292\times2-1398$	+1	
37	5463.5	18298	m	$0_2-292\times2-1398$	−2	diffuse
38	5520.1	18111	w	$0_1-773-1434$	+1	
39	5672.1	17625	w	$0_1-1132-1572$	+12	
40	5684.2	17587	w	$0_2-1132-1572$	+4	
41	5705.0	17524	w	$0_1-1398\times2$	+3	
42	5715.6	17491	w	$0_2-1398\times2$ and	+5	strong
				$0_1-1398-1434$	+6	background
43	5729.5	17449	w	$0_1-1434\times2$ and	0	strong
				$0_2-1398-1434$	−1	background
44	5767.1	17335	mw	$0_1-1398-1599$	+15	diffuse
45	5782.1	17290	mw	$0_2-1398-1599$ and	+5	
				$0_1-1434-1599$	+6	
				0_1-3024	−3	
46	5791.4	17262	w	$0_2-1434-1599$ and/or	+13	
				0_2-3024	+4	
47	5870.7	17029	w	$0_1-292-1398-1599$	+1	
48	5883.8	16991	w	$0_2-292-1398-1599$ or	−2	diffuse
				$0_1-292-1434-1599$	−1	
49	5894.9	16959	w	$0_2-292-1434-1599$	+2	diffuse
50	5948.8	16806	mw	$0_1-481-1434-1599$	+3	
51	5983.1	16709	mw	$0_1-773-1398-1434$	−3	

* reduced to vacuum, ** s — strong, m — medium, w — weak, v — very.

(20100 cm^{-1} in propylene glycol according to [8]). In relation to the 0–0 band, the peaks of the other strong bands are shifted by intervals of 220, 1340 and 1600 cm^{-1}. In crystalline n-octanol the spectrum shows a partly quasilinear structure, like the spectra of absorption and fluorescence.

Decay curves of the phosphorescence of 4,10-DACH diluted solutions ($c \approx 10^{-5}$ M) in hydrocarbon matrices and alcohol glasses show an exponential form. With concentrations $\geqslant 10^{-4}$ M some deviations from the exponential decay were observed in the initial stage (Fig. 5). Such deviations are a characteristic result of reabsorption of the phosphorescence radiation which caused $T_n \leftarrow T_1$ transitions (cf. e. g. [14]). The broad band of the 4,10-DACH triplet-triplet absorption (maximum about 560 nm), described by Bulska et al. [7, 8], comprises the whole range of the phosphorescence spectrum under investigation. This explains the fact that reabsorption of emission occurs even in pretty diluted solutions. The lifetime of the 4,10-DACH phosphorescence in crystalline hydrocarbon matrices (n-C_5H_{12} ÷ n-C_8H_{18}, isooctane, methylcyclohexane) is 1.03 ± 0.02 s, being

in good agreement with the value obtained by Bulska et al. [7, 8]. In frozen normal aliphatic alcohols (from C_2H_5OH to $C_8H_{17}OH$) this time is slightly longer confined within the limits 1.13-1.24 s.

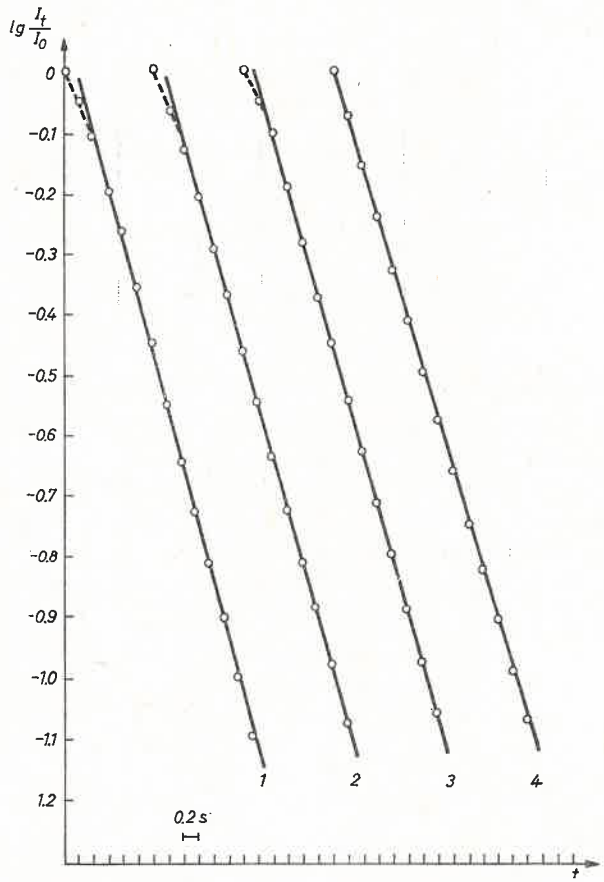

Fig. 5. Decay curves of the phosphorescence of 4,10-DACH in an n-heptane matrix, at 77 K. *1* — $c = 1.10^{-3}$ M, *2* — $c = 5.10^{-4}$ M, *3* — $c = 1.10^{-4}$ M, *4* — $c = 5.10^{-5}$ M

6. Theoretical and discussion

The results obtained point to a similarity of excited S_1, S_2 and T_1 electronic states of 4,10-DACH and chrysene molecules. In the molecules of both compounds they are the π, π^* states and the energies of these states in the 4,10-DACH molecule differ from the energy of the respective states of the chrysene molecule [1–3, 15–18] by no more than 0.03 eV.

The 4,10-DACH molecule belongs, like that of chrysene, to the symmetry point group C_{2h}. The high relative intensity of the 0–0 line in the examined absorption and fluorescence spectra proves that the S_1 (π, π^*) state of the 4,10-DACH molecule belongs to

the B_u-symmetry species, analogously to the S_1 state of chrysene molecule (cf. Table V). Such being the case, in these spectra there should appear mainly the a_g-vibrational modes. The b_g-modes, giving vibronic transitions polarized perpendicular to the plane of the molecule, could have appeared only under the influence of strong perturbations of the

TABLE V

Character table of point group C_{2h}

C_{2h}	E	$C_2(z)$	i	$\sigma_h(xy)$		
A_g	1	1	1	1	R_z	xx, yy, zz, xy
B_g	1	−1	1	−1	R_x, R_y	yz, zx
A_u	1	1	−1	−1	T_z	
B_u	1	−1	−1	1	T_x, T_y	

$S_1(B_u)$ state by the neighbouring $S(n, \pi^*)A_u$ state. However, the structure of the absorption spectrum allows one to suppose the lowest $S(n, \pi^*)$ state of 4,10-DACH molecule to be above the $S_2(\pi, \pi^*)$ state.

The high relative intensity of the 0–0 lines of the 4,10-DACH phosphorescence spectrum testifies to a spin-orbital coupling of $T_1(\pi, \pi^*)B_u$ state (see below) with u-type singlet excited states, most probably mainly with the lowest $^1(n, \pi^*)\, A_u$ state[1].

In case of direct spin-orbit coupling only totally symmetric (a_g) modes should be present in the phosphorescence spectrum. The appearance of out-of-plane b_g-modes could have been caused as well by the first-order spin-vibronic coupling, as — what is more probable — a result of second-order vibronic-spin-orbit coupling occurring according to mechanisms

$$S(\pi, \pi^*)B_u \overset{b_g}{\longleftrightarrow} S(n, \pi^*)A_u \underset{R_x, R_y}{\overset{\text{s.o.}}{\longleftrightarrow}} T_1(\pi, \pi^*)B_u$$

and/or

$$S(\pi, \pi^*)B_u \underset{R_x, R_y}{\overset{\text{s.o.}}{\longleftrightarrow}} T(n, \pi^*)A_u \overset{b_g}{\longleftrightarrow} T_1(\pi, \pi^*)B_u$$

(see Table V).

Out-of-plane vibrations induced by analogous mechanisms of couplings were many a time identified in the phosphorescence spectra of polycyclic diazines (e. g. [20–22]). As pointed out by Hochstrasser [23], second-order vibronic-spin-orbit couplings may also lead to the appearance of u-modes in symmetry allowed $T(u) \rightarrow S(g)$ transitions, but the intensity of respective vibronic transitions should be extremely weak.

To establish the symmetry of vibrations identified in the electronic spectra of 4,10-DACH, we examined the Raman spectrum of this compound, determining the de-

[1] In this work the polarization spectra were not examined and the polarization of 0–0 transition in the phosphorescence spectrum was not determined. However, it can be supposed to be polarized perpendicular to the molecule plane, like it is in other hitherto examined polycyclic azines in $T_1(\pi, \pi^*)$ state (cf. e. g. [19]).

polarization degree of the bands. For the measurements of polarization a benzene solution of 4,10-DACH was used. We also registered the Raman spectrum of a polycrystalline sample of the compound tested, which helped to find the bands in the spectrum of the solution deformed by a partial overlapping of the bands of benzene Raman spectrum.

TABLE VI

Fundamental vibration frequencies for the S_0 and S_1 states of 4,10-DACH molecule (in cm^{-1})

$S_1 \leftarrow S_0$	$S_1 \rightarrow S_0$	$T_1 \rightarrow S_0$	Raman*
285	293	292	292 a_g
—	383	389	390 a_g
472	483	481	480 a_g
645	675	679	678 a_g
771	777	773	780 a_g
—	893	—	887 a_g
1038	1037	—	1035 a_g
—	—	1132	1125 ?
—	1298	1300	1299 a_g
1392	1402	1398	1398 a_g
1418	1433	1434	1437 a_g
1568	—	1572	1570 ?
—	—	1599	1600 ?

* in benzene solution at room temperature.

Table VI shows the frequencies of Raman bands corresponding to the fundamental vibration frequencies identified as a result of the analysis of quasilinear electronic spectra of 4,10-DACH. It can be seen that all vibrations active in the electronic spectra are also active in the Raman spectrum, thus belonging to *g*-modes. In almost all cases the depolarization degree proved the a_g-symmetry of vibrations. The experimental conditions did not render it possible to state this directly for the vibrations 1125 cm^{-1} (weak, diffuse band) as well as 1570 and 1600 cm^{-1} (the band intensities adulterated due to the overlapping of the Raman bands of benzene). However, it must be pointed out that vibrations of similar frequencies, occurring in the Raman spectra of polycyclic aromatic hydrocarbons, belong to totally symmetric skeletal vibrations.

Thus, the phosphorescence of 4,10-DACH seems to occur due to a direct spin-orbit mechanism. In the spectrum examined there certainly do not appear any out-of-plane C-H bending modes, which are very characteristic of the phosphorescence spectra of polycyclic 1,4-diazines [20–22, 24]. It should be emphasized that in the IR-spectrum of 4,10-DACH, examined in [6] and also obtained pending this research, there appears a strong band 770 cm^{-1} which can be ascribed to an out-of-plane hydrogen wagging vibration in the sets of three neighbouring groups of CH present in the terminal rings of 4,10-DACH molecule [6]. This is, however, a vibration belonging to *u*-modes. The presence of rather strong vibronic transitions with participation of *u*-modes in the electronic spectra

examined by us could not be explained by any reasonable mechanism of couplings. Besides, the vibration at about 770 cm^{-1} is also characteristic of the emission spectra of chrysene [3], in the molecule of which three CH groups are nowhere neighbouring (there are only sets including two and four CH groups). Therefore, we are justified in stating that the fundamental frequency 771–777 cm^{-1} observed in the electronic spectra of 4,10-DACH, corresponds to vibration 780 cm^{-1} (a_g) identified in the Raman spectrum, and not to vibration 770 cm^{-1} (a_u) active in the IR-spectrum of this compound.

As it results from the vibrational analyses of the spectra examined, the fundamental vibration frequencies of the 4,10-DACH molecule in the S_0, S_1 and T_1 states have very similar values (Table VI); no longer progressions were observed in the spectra, maybe with the exception of the progression of the 293 cm^{-1} vibration in the fluorescence spectrum (cp. Table III). So it seems that the geometry of the molecule in excited states S_1 and T_1 does not significantly differ from its geometry in the ground state. Contrary to the molecules of some other polycyclic diazines [10, 26], no spectral features point to out-of-plane distortions of the 4,10-DACH molecule in the lowest excited states.

The calculation of π-electronic structure of 4,10-DACH has been performed by the semiempirical PPP method [27, 28] including configuration interaction (CI). In CI, all singly excited configurations which include six upper occupied and six lowest unoccupied orbitals were taken into account.

The one-center repulsion integrals were estimated as I–A, where I and A are the ionization potential and the electron affinity, respectively. The values of I and A for carbon and nitrogen atoms were taken from the table given by Hinze and Jaffe [29].

Two-center repulsion integrals were approximated with the Mataga-Nishimoto formula [30]. The core resonance integrals were represented by the Katagiri-Sandorfy relation [31]. The lowest n, π^* electronic states were calculated independently, according to the Inuzuka-Becker scheme [32].

In the calculation it has been assumed that 4,10-DACH molecule consist of regular hexagons with every C–C and C–N bond length equal to 1.40 Å.

The calculated energies of the π^*–π and π^*–n transitions together with corresponding oscillator strengths are compared with the experimental results in Table VII.

TABLE VII

The lowest π, π^* and n, π^* electronic states of 4,10-DACH

States	Singlet excitation energies (eV)		Oscillator strengths calc.	States	Triplet excitation energies (eV)	
	calc.	obs.			calc.	obs.
$B_u(\pi, \pi^*)$	3.33	3.43	0.297	$B_u(\pi, \pi^*)$	1.78	2.52
$B_u(\pi, \pi^*)$	3.75	3.86	0.165	$A_g(\pi, \pi^*)$	2.46	
$A_u(n, \pi^*)$	3.79			$B_u(\pi, \pi^*)$	2.85	
$A_g(\pi, \pi^*)$	4.22		0.000	$A_u(n, \pi^*)$	3.27	
$A_g(\pi, \pi^*)$	4.28		0.000			
$B_u(\pi, \pi^*)$	4.60	4.7 [6]	2.072			

As can be seen, the compatibility of experimentally determined and calculated energies of the states $S_1(\pi, \pi^*)$ and $S_2(\pi, \pi^*)$ is very good. The calculations have also confirmed the lowest singlet state n, π^* to be slightly above the state $S_2(\pi, \pi^*)$ (see above). Now, the energies of triplet states, calculated with the method used in this research, appear to be decidedly too low. Undoubtedly, this concerns also the lowest $^3(n, \pi^*)$ state which, according to calculations, would have slightly lower energy than the $S_1(\pi, \pi^*)$ state. However, the quantum yield of 4,10-DACH fluorescence is 0.23 [33] even at room temperature, thus being equal to the quantum yield of chrysene fluorescence at 77 K [34]. If in the 4,10-DACH molecule the $^3(n, \pi^*)$ state was below the $S_1(\pi, \pi^*)$ state, then the quantum yield of fluorescence of this compound would have been considerable decreased as compared with chrysene due to a high rate of the intersystem crossing process $^1(\pi, \pi^*) \rightsquigarrow {}^3(n, \pi^*)$ (cp. e. g. [19]). Therefore, it seems that the lowest $^3(n, \pi^*)$ state of the 4,10-DACH molecule has a higher energy than its $S_1(\pi, \pi^*)$ state.

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REFERENCES

[1] R. N. Nurmukhametov, E. G. Popova, N. S. Dokunikhin, *Opt. Spektrosk.* **9**, 593 (1960); **11**, 134 (1961).
[2] T. N. Bolotnikova, O. F. Elnikova, *Opt. Spektrosk.* **36**, 292 (1974).
[3] A. Olszowski, Z. Kubiak, *Bull. Acad. Pol. Sci., Sér. Sci. Math. Astron. Phys.* **23**, 641 (1975); *Bull. Acad. Pol. Sci., Sér. Sci. Math.* **23**, 921 (1975).
[4] K. Shibata, *Bull. Chem. Soc. Jap.* **24**, 187 (1951).
[5] J. A. Baltrop, K. E. McPhee, *J. Chem. Soc.* **1952**, 638.
[6] C. V. Nekrasov, A. V. Elcov, *Zh. Org. Khim.* **7**, 188 (1971).
[7] H. Bulska, A. Chodkowska, A. Grabowska, *Chem. Phys. Lett.* **12**, 508 (1972).
[8] H. Bulska, Dissertation, Institute of Physical Chemistry, Polish Academy of Sciences, Warszawa 1974.
[9] D. J. Morantz, T. E. Martin, *Trans. Faraday Soc.* **65**, 665 (1969).
[10] K. Brenner, Z. Ruziewicz, *J. Lumin.* **15**, 235 (1977).
[11] Z. Ruziewicz, *Acta Phys. Pol.* **28**, 389 (1965).
[12] E. V. Shpolskii, *Usp. Fiz. Nauk* **71**, 215 (1960); **77**, 321 (1962); **80**, 255 (1963).
[13] T. N. Bolotnikova, O. F. Elnikova, *Opt. Spektrosk.* **36**, 895 (1974).
[14] Z. Ruziewicz, J. F. Timofeeva, *Bull. Acad. Pol. Sci., Sér. Sci. Math. Astron. Phys.* **19**, 1135 (1971).

[15] R. S. Becker, I. S. Singh, E. A. Jackson, *J. Chem. Phys.* **38**, 2144 (1963).
[16] E. I. Al'shits, R. I. Personov, B. M. Kharlamov, *Opt. Spektrosk.* **41**, 803 (1976).
[17] R. L. Hummel, K. Ruedenberg, *J. Phys. Chem.* **66**, 2334 (1962).
[18] M. Mestechkin, L. Gutyrya, V. Poltavets, *Opt. Spektrosk.* **28**, 454 (1970).
[19] S. K. Lower, M. A. El-Sayed, *Chem. Rev.* **66**, 199 (1966).
[20] E. C. Lim, J. M. H. Yu, *J. Chem. Phys.* **49**, 3878 (1968).
[21] H. Chojnacki, A. Olszowski, Z. Ruziewicz, *J. Mol. Struct.* **5**, 297 (1970).
[22] K. Brenner, Z. Ruziewicz, 2nd Polish Conf. Luminescence, Toruń, September 1974, vol. A, *Luminescence of Organic Substances*, p. 17.
[23] R. M. Hochstrasser, *Molecular Aspects of Symmetry*, W. A. Benjamin Inc., New York 1966.
[24] N. Kanamaru, E. C. Lim, *J. Chem. Phys.* **62**, 3252 (1975).
[25] E. C. Lim, R. Li, Y. H. Li, *J. Chem. Phys.* **50**, 4925 (1969).
[26] E. C. Lim, Y. H. Li, *Chem. Phys. Lett.* **4**, 25 (1969).
[27] R. Pariser, R. G. Parr, *J. Chem. Phys.* **21**, 466, 767 (1953).
[28] J. A. Pople, *Trans. Faraday Soc.* **49**, 1375 (1953).
[29] J. Hinze, H. H. Jaffe, *J. Am. Chem. Soc.* **34**, 540 (1962).
[30] N. Mataga, K. Nishimoto, *Z. Phys. Chem. N. F.* **13**, 140 (1957).
[31] T. Ohta, H. Kuroda, T. L. Kunii, *Theor. Chim. Acta* **19**, 167 (1970).
[32] K. Inuzuka, R. S. Becker, *Bull. Chem. Soc. Jap.* **45**, 1557 (1972).
[33] A. Grabowska, private communication.
[34] R. Li, E. C. Lim, *J. Chem. Phys.* **57**, 605 (1972).