SPECTRAL PROPERTIES OF ZEROMETHINEMEROCYANINES

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Twenty six zeromethinemerocyanine dyes *III* were prepared by condensation of carbonylmethylene group containing heterocycles *II* with nitrogen-containing 2-alkylmercapto heterocycles *I*. Their absorption maxima in the visible spectral region in ethanolic solution, as well as of the dyes adsorbed on silver halide, were measured. IR spectra in chloroform and in KBr were also studied.

In the present study we synthesised 26 zeromethinemerocyanines *III* by condensation of carbonyl group-containing heterocycles *II* with 2-alkylmercapto heterocycles, containing a nitrogen atom *I*. These dyes have been described in patent literature[1-7] as sensibilisers in photographic silver halide emulsions in the region about 400 to 500 nm. Spectral properties of these compounds are evaluated and their physical and photochemical properties as function of their structure are systematically studied. The zeromethinemerocyanines were prepared according to Kendall[8].

TABLE I
Dyes *III* (Z^2 = 3-ethylrhodanine, Z^1 = benzothiazole)

Dye	R^1 R^2	Yield, % m. p., °C	Formula (mol. w.)	Calculated/Found % C	 % H	 % N	 % S
1	CH_3 H	38·8 279—280	$C_{13}H_{12}N_2OS_3$ (308·4)	50·62 50·41	3·92 4·01	9·08 9·25	31·19 31·37
2	C_3H_7 H	82·35 280—281	$C_{15}H_{16}N_2OS_3$ (336·4)	53·38 53·07	4·78 4·94	8·30 8·16	28·50 28·71
3	C_2H_5 CH_3O	76·2 232—233	$C_{15}H_{16}N_2O_2S_3$ (352·4)	51·11 50·95	4·58 4·43	7·95 7·82	27·29 27·59
4	C_2H_5 NO_2	43·2 105—106	$C_{14}H_{13}N_3O_3S_3$ (367·4)	45·76 45·43	3·57 3·53	11·43 11·37	26·18 26·26

EXPERIMENTAL

Melting points were determined on a Kofler block after drying the samples over phosphorus pentoxide at 80°C and 0·2 Torr. For the measurements and elemental analyses the dyes were purified by chromatography. The dye (0·2 g) was dissolved in chloroform (150 ml) and chromatographed on neutral alumina (Reanal, Brockmann activity II). The chloroform eluate was taken down and the dye crystallised from ethanol. The yields, physical constants and other data are given in Table I and II.

TABLE II

Dyes *III* (R^1 = ethyl, R^2 = H)

Dye	Z^1 Z^2	Yield, % m. p., °C	Formula mol. w.	Calculated/Found			
				% C	% H	% N	% S
5	benzoxazole	71·24	$C_{14}H_{14}N_2O_2S_2$	54·88	5·80	9·14	20·93
	3-ethylrhodanine	174—175	(306·4)	54·80	5·83	9·03	21·04
6	benzthiazole	34·4	$C_{14}H_{14}N_2OS_3$	52·14	4·38	8·69	29·83
	3-ethylrhodanine	143—146	(322·5)	51·78	4·56	8·41	29·84
7	2-quinoline	76·2	$C_{16}H_{16}N_2OS_2$	60·73	5·10	8·85	20·27
	3-ethylrhodanine	195—197	(316·4)	60·52	5·32	9·01	20·19
8	4-methylthiazole	36·4	$C_{11}H_{14}N_2OS_3$	46·12	4·93	9·78	33·58
	3-ethylrhodanine	164—166	(288·4)	45·85	5·05	9·51	33·76
9	4-quinoline	18·4	$C_{16}H_{14}N_2OS_2$	60·73	5·10	8·85	20·27
	3-ethylrhodanine	204—205	(314·4)	60·45	5·05	8·56	20·31
10	2-pyridine	36·3	$C_{12}H_{14}N_2OS_2$	54·10	5·30	10·52	24·07
	3-ethylrhodanine	151—153	(266·3)	54·37	5·47	10·42	24·14
11	4-pyridine	56·5	$C_{12}H_{14}N_2OS_2$	54·10	5·30	10·52	24·07
	3-ethylrhodanine	257—258	(266·3)	54·23	5·52	10·39	23·83
12	benzoxazole	62·5	$C_{14}H_{14}N_2O_3S$	57·91	4·86	9·65	11·04
	3-ethyl-4-oxo-2-thione	181—182	(290·3)	57·86	4·80	9·33	11·49
13	benzoxazole	30·8	$C_{14}H_{15}N_3O_2S$	58·11	5·23	14·52	11·08
	1,3-dimethylthiohydantoin	170—172	(289·3)	57·79	5·42	14·25	11·42
14	benzoxazole	20·5	$C_{19}H_{17}N_3O_2$	71·46	5·37	13·15	
	1-fenyl-3-methyl-5-pyrazolone	158—159	(319·4)	71·16	5·65	13·11	
15	benzthiazole	40·3	$C_{14}H_{14}N_2O_2S_2$	54·88	4·61	9·14	20·93
	3-ethyl-4-oxo-	214—215	(306·4)	54·50	4·78	9·05	20·95
16	benzthiazole	70·9	$C_{14}H_{15}N_3OS_2$	55·05	4·95	13·76	21·00
	1,3-dimethyl-	214—215	(305·4)	54·87	4·85	13·58	21·20
17	benzthiazole	26·3	$C_{19}H_{17}N_3OS$	68·03	5·11	12·53	9·56
	1-fenyl-3-methyl-5-pyrazolone	149—150	(335·4)	68·10	5·36	12·76	9·32
18	2-quinoline	36·4	$C_{16}H_{16}N_2O_2S$	63·98	5·37	9·33	10·67
	3-ethyl-4-oxo-2-thione	199—200	(300·4)	64·04	5·52	9·22	10·96

TABLE II
(*continued*)

Dye	Z^1 Z^2	Yield, % m. p., °C	Formula mol. w.	Calculated/Found			
				% C	% H	% N	% S
19	2-quinoline	62·2	$C_{16}H_{17}N_3OS$	64·19	5·72	14·04	10·71
	1,3-dimethylthiohydantoin	203—204	(299·4)	64·07	5·84	14·35	11·05
20	2-quinoline	28·5	$H_{21}H_{19}N_3 2$	4·57	5·81	12·76	—
	1-fenyl-3-methyl-5-pyrazolone	241—242	(329·4)	76·43	5·84	12·71	—
21	4-methylthiazole	36·2	$H_{11}H_{14}N_2O_2S_2$	48·87	5·22	10·36	23·72
	3-ethyl-4-oxo-2-thione	263—264	(270·4)	48·60	5·14	10·18	24·01
22	4-methylthiazole	27·7	$C_{11}H_{15}N_3OS_2$	49·04	5·62	15·60	23·81
	1,3-dimethylthiohydantoin	179—181	(269·4)	49·56	5·71	15·66	23·98
23	4-methylthiazole	56·9	$C_{16}H_{17}N_3OS$	64·19	5·73	14·04	10·71
	1-fenyl-3-methyl-5-pyrazolone	174—175	(299·4)	63·87	5·94	13·91	10·57
24	4-pyridine	36·9	$C_{12}H_{14}N_2O_2S$	57·58	5·64	11·19	12·81
	3-ethyl-4-oxo-2-thione	232—233	(250·3)	57·86	5·52	11·07	13·00
25	4-pyridine	52·00	$C_{12}H_{15}N_3OS$	57·80	6·06	16·86	12·86
	1,3-dimethylthiohydantoin	228—229	(249·3)	57·88	6·37	16·46	13·14
26	4-pyridine	59·6	$C_{17}H_{17}N_3O$	73·09	6·13	15·04	—
	1-fenyl-3-methyl-5-pyrazolone	240—242	(279·3)	72·90	6·03	14·95	—

Spectrophotometric Measurements

The absorption maxima (Table III) were measured on CF4 Optica Milano recording spectrophotometer in 1 cm cells in $1 \cdot 10^{-5}$ mol/l ethanolic solutions. The concentrations of the measured solutions were within the limits of validity of Lambert–Beer law. The IR spectra were taken on a UR 10 (Zeiss, Jena) spectrophotometer in 1% (wt) chloroform solutions; when measured in KBr, the KBr pills contained 1 mg dye per 200 mg KBr.

Characteristics of the Photographic Emulsion Employed

We used a positive non-washed silver chloride–bromide gelatinous photographic emulsion, containing 12·7 g Ag/kg emulsion, 44·6 mol% Ag in the silver halides grain, 0·071 g Cd/1 g Ag, 45 mol% of free NaCl, 7·2% of gelatine, stabilised by $3 \cdot 10^{-4}$ g of 3-mercapto-5-imino-1,5-dihydro-4,1,2-thiodiazole/1 g Ag. The absorption curves were taken on an SF 10 recording spectrophotometer.

RESULTS AND DISCUSSION

Effect of the character of heterocyclic nuclei: The bathochromic shift of the absorption maximum in the visible region increases in the following order (Fig. 1): benzoxazole < < benzothiazole < 4-methylthiazole < 2-pyridine < 4-pyridine < 2-quinoline < < 4-quinoline. This order agrees with results obtained with other types of polymethine dyes[9-14]. A larger bathochromic shift is observed with dyes containing 2-quinoline and 4-quinoline nuclei.

It is known from deviation measurements[10] that the structure of most merocyanines can be expressed by the non-polar formula. Therefore an increase in the relative basicity of the heterocyclic nucleus brings about a shift to the dipolar structure manifesting itself by the bathochromic shift. An increasing bulk of substituent on the benzothiazole nitrogen atom causes no marked absorption maximum shift; on the other hand, an introduction of a methoxy or a nitro group into the position 6 of the benzothiazole nucleus is accompanied by a bathochromic shift.

In the spectra of zeromethinemerocyanines with a given constant heterocycle (benzoxazole, benzothiazole, 4-methylthiazole, 2-quinoline, 4-quinoline, 2-pyridine, 4-pyridine), variation in the heterocycles, containing a carbonylmethylene group, results in a hypsochromic shift, which increases in the following order: 3-ethylrhodanine < 1,3-dimethylthiohydantoin < 3-ethyl-4-oxo-2-thione < 1-phenyl-3-methyl-5-pyrazolone. Except for the 3-ethylrhodanine nucleus, the same order was found by various authors[10,15-19] on the basis of deviation measurements with the use of the Foster rule in the study of relative "acidities".

The absorption curves of the dyes, adsorbed on the silver halide, were obtained by reflection measurements on emulsion layers with the adsorbed sensibiliser against the nonsensibilised layer. The differences between the thus-obtained absorption

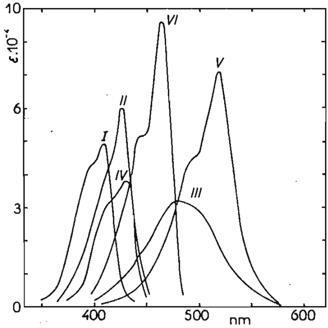

FIG. 1

Absorption Curves of Zeromethinemerocyanines with 3-Ethylrhodanine Nucleus and Various Heterocycles (in ethanol)

I 3-Ethylbenzoxazole, *II* 3-ethylbenzothiazole, *III* 1-ethyl-2-quinoline, *IV* 3-ethyl-4-methylthiazole, *V* 1-ethyl-4-quinoline, *VI* 1-ethyl-2-pyridine.

maxima and the maxima observed in solutions are analogous to those for the solvatochromic effect (Table III). In the spectra of dyes, containing 3-ethylrhodanine nuclei with methyl, ethyl or isopropyl attached to the nitrogen atom, the bathochromic shift increases in the order methyl < isopropyl < ethyl. For substituents at the position 6 of the benzothiazole ring the bathochromic shift is greater for NO_2 than for CH_3O. The hypsochromic shifts for zeromethinemerocyanines with different heterocyclic nuclei, containing carbonylmethylene group (Z^2), are rather irregular. The spectra of most of the 1-phenyl-3-methyl-5-pyrazolone-containing dyes exhibited

TABLE III

Absorption Maxima (nm) of the Dyes *III* in Ethanolic Solution and Adsorbed on Silver Halide

Dye	λ_{max} in ethanol	$\varepsilon \, . \, 10^{-4}$ l mol^{-1} cm^{-1}	λ_{max} on AgHal	$\Delta\lambda_{max}$[a]
1	(410), 428	2·1, 3·3	435	7
2	(412), 429	3·0, 4·5	460	31
3	(420), 437	4·5, 6·1	448	11
4	(425), 443	2·3, 3·1	484	41
5	(398), 410	4·3, 4·86	448	38
6	(412), 429	4·45, 6·0	466	37
7	(452), 480, (498)	2·0, 3·1, 3·0	517	37
8	(414), 431	3·25, 3·8	464	33
9	(460), (492), 518	1·4, 4·5, 7·1	548	30
10	463	3·53	476	13
11	(420), 444, 464	2·0, 5·02, 8·65	458	−6
12	372, 383	5·24, 5·02	—	—
13	(380), 392	4·7, 5·53	415	23
14	342	2·5	—	—
15	405	5·95	440	35
16	425	3·5	436	9
17	378	1·78	—	—
18	(402), 426, 448, 454	1·0, 2·5, 3·4, 2·4	484	30
19	509	2·03	520	11
20	462	1·1	470	8
21	400, 411	3·72, 3·94	440	24
22	429	1·06	448	19
23	377	0·9	—	—
24	(400), 417, 440	2·8, 5·7, 7·6	443	3
25	(440), 457	4·7, 4·8	455	−2
26	320, 394	1·2, 2·29	—	—

[a] $\Delta\lambda = \lambda_{max}$ (on AgHal) − λ_{max} (in ethanol).

TABLE IV

Infrared Spectra of the Dyes *III* (in KBr)

s Strong, m medium, w weak, vw very weak, sh shoulder.

Dye	ν, cm^{-1} [a]
1	507 m, 532 w, 750 m, 837 w, 882 m, 998 w, 1 052 w, 1 123 m, 1 180 w, 1 235 s, 1 272 w, 1 315 m, 1 352 s, 1 400 m, 1 420 m, 1 508 sh, 1 518 s, 1 638 m
2	838 w, 884 m, 900 w, 998 w, 1 055 w, 1 127 m, 1 183 w, 1 240 s, 1 277 w, 1 318 w, 1 356 m, 1 405 m, 1 425 m, 1 457 w, 1 480 w, 1 520 s, 1 642 m
3	511 w, 747 w, 799 m, 869 w, 900 w, 1 035 w, 1 121 m, 1 179 m, 1 222 s, 1 242 m, 1 280 m, 1 316 m, 1 354 m, 1 402 w, 1 448 w, 1 478 s, 1 518 s, 1 608 w, 1 652 m
4	515 w, 552 w, 688 w, 723 w, 749 sh, 758 m, 835 m, 901 m, 1 001 m, 1 066 m, 1 123 m, 1 176 w, 1 237 m, 1 275 m, 1 332 s, 1 410 m, 1 432 s, 1 481 w, 1 525 s, 1 574 w, 1 601 w, 1 654 w
5	505 m, 575 w, 755 s, 801 w, 888 m, 996 w, 1 122 s, 1 170 w, 1 242 s, 1 320 w, 1 401 w, 1 442 sh, 1 489 m, 1 575 s, 1 643 w, 1 675 s
6	512 m, 755 m, 800 w, 880 m, 900 w, 1 035 w, 1 057 w, 1 098 w, 1 122 s, 1 181, 1 230 s, 1 248 sh, 1 318 m, 1 352 m, 1 507 w, 1 457 sh, 1 473 m, 1 518 s, 1 650 s
7	510 w, 697 w, 742 w, 769 m, 821 m, 902 m, 980 w, 1 122 s, 1 170 s, 1 233 s, 1 320 sh, 1 342 s, 1 402 s, 1 444 s, 1 488 s, 1 518 w, 1 573 s, 1 619 s, 1 646 sh
8	518 w, 542 w, 708 w, 742 w, 886 m, 1 002 w, 1 096 m, 1 127 s, 1 188 w, 1 239 s, 1 315 sh, 1 333 sh, 1 349 s, 1 378 sh, 1 400 m, 1 452 sh, 1 468 s, 1 508 s, 1 603 sh, 1 625 s
9	506 w, 530 m, 700 w, 756 s, 778 sh, 794 w, 830 m, 920 w, 1 014 w, 1 055 m, 1 090 m, 1 120 s, 1 168 m, 1 244 s, 1 275 sh, 1 330 s, 1 360 w, 1 408 s, 1 432 s, 1 462 m, 1 521 w, 1 558 s, 1 602 w, 1 651 s
10	530 w, 742 w, 773 s, 812 w, 828 w, 894 w, 1 072 m, 1 095 m, 1 120 s, 1 152 s, 1 237 s, 1 288 w, 1 318 m, 1 357 s, 1 381 m, 1 402 m, 1 447 s, 1 480 s, 1 512 sh, 1 551 s, 1 608 s, 1 636 m
11	505 w, 527 w, 567 w, 595 w, 748 w, 809 m, 838 m, 884 w, 1 088 w, 1 128 m, 1 153 m, 1 202 s, 1 240 s, 1 320 w, 1 369 m, 1 390 s, 1 421 m, 1 441 w, 1 533 s, 1 615 s, 1 660 m
12	490 m, 539 m, 645 w, 700 w, 756 m, 800 w, 962 m, 1 001 m, 1 020 w, 1 094 m, 1 129 s, 1 255 s, 1 288 s, 1 350 s, 1 385 m, 1 422 m, 1 473 m, 1 618 s, 1 652, 1 708 m
13	497 s, 586 w, 696 m, 702 m, 757 m, 798 w, 850 w, 894 w, 960 w, 1 036 s, 1 101 m, 1 126 s, 1 170 m, 1 261 m, 1 338 s, 1 398 s, 1 457 m, 1 486 s, 1 593 s, 1 643 m, 1 691 s
14	512 w, 596 w, 634 w, 656 m, 693 m, 738 m, 760 m, 821 w, 910 w, 970 w, 1 020 m, 1 004 m, 1 051 m, 1 105 m, 1 132 m, 1 147 m, 1 186 w, 1 269 s, 1 318 m, 1 348 s, 1 400 m, 1 487 s, 1 579 s, 1 658 s
15	515 m, 724 w, 754 m, 809 w, 868 w, 964 w, 993 m, 1 132 w, 1 164 m, 1 236 m, 1 255 m, 1 281 s, 1 352 s, 1 385 s, 1 420 m, 1 456 m, 1 510 w, 1 578 s, 1 608 s, 1 652 w, 1 696 m
16	502 m, 594 w, 669 w, 741 w, 759 m, 787 w, 842 w, 947 w, 1 013 w, 1 040 w, 1 060 w, 1 140 m, 1 308 m, 1 361 m, 1 472 m, 1 538 s, 1 590 w, 1 660 m

TABLE IV
(*Continued*)

Dye	ν, cm^{-1} [a]
17	512 w, 545 w, 588 w, 637 m, 658 m, 697 m, 767 s, 822 m, 912 w, 980 w, 1 011 m, 1 038 m, 1 059 w, 1 080 w, 1 155 w, 1 245 m, 1 342 s, 1 468 s, 1 483 s, 1 505 s, 1 595 m, 1 626 s
18	520 w, 569 w, 739 w, 764 m, 820 w, 971 m, 1 010 m, 1 077 m, 1 135 m,1 169 s, 1 222 m, 1 259 m, 1 288 s, 1 345 s, 1 362 s, 1 422 m, 1 455 m, 1 507 m, 1 549 s, 1 626w, 1 675 m
19	741 m, 760 w, 830 w, 945 w, 1 030 m, 1 059 w, 1 152 m, 1 180 m, 1 232 w, 1 368 s, 1 392 s, 1 457 m, 1 500 s, 1 540 s, 1 570 m, 1 619 s, 1 661 s
20	502 w, 514 w, 528 w, 618 w, 651 m, 694 m, 732 w, 750 m, 769 m, 788 w, 844 m, 872 w, 911 w, 1 004 m, 1 035 m, 1 070 m, 1 138 w, 1 167 m, 1 255 w, 1 304 m, 1 352 s, 1 447 s, 1 489 s, 1 527 s, 1 565 m, 1 605 s, 1 625 s,
21	511 m 544 w, 617 w, 743 w, 803 w, 871 w, 960 w, 990 m, 1 088 w, 1 106 w, 1 136 w, 1 165 m, 1 200 w, 1 283 s, 1 349 m, 1 382 m, 1 421 m, 1 464 m, 1 507 m, 1 558 s, 1 606 w, 1 668 s
22	507 m, 541 w, 586 w, 630 w, 682 w, 741 m, 791 w, 854 w, 914 w, 962 w, 1 019 m, 1 050 m, 1 135 m, 1 158 m, 1 178 w, 1 252 w, 1 316 m, 1 358 s, 1 389 s, 1 449 m, 1 484 s, 1 530 s, 1 594 w, 1 662 s
23	788 m, 830 w, 947 w, 982 w, 1 011 w, 1 060 w, 1 341 m, 1 361 m, 1 378 s, 1 403 s, 1 598 w, 1 621 s
24	501 m, 516 w, 746 w, 823 m, 965 w, 988 w, 1 169 w, 1 198 s, 1 087 w, 1 287 s, 1 348 s, 1 418 m, 1 440 w, 1 466 w, 1 522 w, 1 571 s, 1 632 s, 1 648 m
25	497 s, 514 m, 588 w, 653 w, 700 w, 751 w, 819 m, 839 m, 946 m, 1 009 s, 1 041 w, 1 095 m, 1 198 s, 1 297 m, 1 350 s, 1 388 s, 1 431 s, 1 486 s, 1 539 s, 1 610 s, 1 671 s
26	516 w, 587 w, 640 w, 652 w, 701 w, 726 w, 841 m, 1 006 s, 1 029 w, 770 m, 1 194 s, 1 221 m, 1 332 s, 1 431 s, 1 489 s, 1 519 s, 1 604 s, 1 647 s

no maximum. The spectra of dyes, adsorbed on silver halide in the photographic emulsion, did not reveal formation of aggregates. The absorption maxima shifts were obviously caused by the polarising effect of the silver halide in the emulsion. Of papers on infrared spectra of polymethine dyes[20-22], the work of Nys and Janssen[23] is interesting: it concerns the relation between the carbonyl group polarisation and the frequency of its absorption band in the IR spectra of merostyryl and merocyanine dyes. With an increasing polarisation, the C=O bond has an increasing single bond character and the absorption maximum is therefore shifted to lower frequencies. On the other hand, depolarisation of this band is accompanied by a shift toward higher frequencies. We studied now carbonyl frequencies in the IR spectra for various dye molecules (Table IV). The effect of carbonyl group polarisation on the band wavenumber was confirmed for dyes, containing 3-ethylrhodanine nucleus in combination with benzoxazole or benzothiazole: the dye with benzothiazole ring exhibited carbonyl band at lower wavenumber. The same effect was observed with zeromethinemerocyanines with 3-ethylrhodanine ring and benzothiazole or 4-methylthiazole nuclei. Extension of conjugation was accompanied by a shift of the carbonyl band toward higher wavenumbers for the dyes with 3-ethylrhodanine and quinoline rings, linked in positions 2 and 4. This kind of shift was also observed for zeromethinemerocyanines with 3-ethylrhodanine nucleus combined with a pyridine nucleus in position 2 or 4.

For zeromethinemerocyanines, containing "constant" heterocyclic "basic" nuclei with a nitrogen atom, and various heterocycles with carbonylmethylene group, the following order has been found: 1-phenyl-3-methyl-5-pyrazolone < 3-ethylrhodanine < 1,3-dimethylthiohydantoin < 3-ethyl-4-oxo-2-thione. This order corresponds to the relative "acidity" sequence of the mentioned heterocyclic derivatives found by other methods (deviation, Foster rule)[10,15-19]. Substituents in the position 6 of the benzothiazole nucleus, as well as substituents at the nitrogen atom, do not significantly affect the position of the C=O absorption band in the 3-ethylrhodanine nucleus. The frequencies of 3-ethylrhodanine, 3-ethyl-4-oxo-2-thione, 1,3-dimethylthiohydantoin and 1-phenyl-3-methyl-5-pyrazolone are given in Table V.

The double bond, connecting both the heterocyclic nuclei, manifests itself by bands at about 1596–1640 cm^{-1}, overlapping with the carbonyl band in the benzothiazole dyes. Measurements in chloroform on a high resolution instrument separated the C=C band at about 1600 cm^{-1} from the C=O band at about 1640 cm^{-1}.

TABLE V

Infrared Spectra of Heterocyclic Compounds, Containing Carbonylmethylene Group
s Strong, m medium, w weak, vw very weak.

Compound	ν, cm^{-1}
3-Ethylrhodanine	493 m, 544 w, 598 w, 651 m, 778 w, 949 w, 1 132 s, 1 247 s, 1 351 s, 1 442 m, 1 682 m, 1 737 s
3-Ethyl-4-oxo-2-thione	508 vw, 542 m, 563 w, 661 m, 675 m, 969 m, 792 m, 960 m, 1 008 m, 1 090 m, 1 114 s, 1 178 s, 1 249 m, 1 290 s, 1 390 s, 1 545 w, 1 670 m, 1 764 s
1,3-Dimethylthiohydantoin	493 m, 589 m, 649 m, 676 m, 866 m, 980 s, 1 059 m, 1 102 s, 1 139 s, 1 187 m, 1 331 s, 1 380 s, 1 249 s
1-Fenyl-2-methyl-5-pyrazolone	503 w, 590 w, 692 m, 754 m, 844 w, 1 044 w, 1 085 w, 1 162 w, 1 200 w, 1 319 m, 1 377 s, 1 408 m, 1 466 w, 1 505 s, 1 568 s, 1 620 s, 1 728 m

The intensity and mutual position of both these bands show well the effect of conjugation and coplanarity of both substituents. For perfectly coplanar systems such as those with quinoline nucleus, the band due to the double bond is well developed whereas in systems where this bond is not conjugated with the substituent, the band intensity is small (Table VI). This effect can be used as a criterion for assessing the degree of conjugation and coplanarity of both systems in the molecule.

TABLE VI

Values of ν(C=C) and ν(C=O) (in cm^{-1}) for Compounds 1–26
s Strong, m medium, w weak, vw very weak.

Dye	C=C (KBr)	C=O (KBr)	C=C ($CHCl_3$)	C=O ($CHCl_3$)
1	—	1 638 m	1 602 w	1 646 m
2	—	1 642 m	1 605 w	1 649 m
3	1 608 vw	1 652 m	1 606 w	1 642 m
4	1 601 w	1 654 w	1 602 m	1 658 w
5	1 643 w	1 675 s	1 637 vw	1 663 m
6	—	1 650 s	1 604 vw	1 647 m
7	1 619 s	1 646 sh	1 614 s	1 643 m
8	1 603 sh	1 625 s	1 604 vw	1 630 m
9	1 602 s	1 651 s	1 596 s	1 646 w
10	1 608 s	1 636 m	1 617 m	1 638 s
11	1 615 s	1 660 m	1 607	1 664 m
12	1 652 m	708 m	1 643 m	1 707 m
13	1 643 m	1 691 s	1 641,	1 689 m
14	1 579 s	1 658 s	1 596 m	1 650 s
15	1 652 vw	1 696 m	1 650 w	1 689 w
16	1 590 vw	1 660 m	1 598 w	1 668 m
17	1 595 m	1 626 s	1 594 w	1 622 m
18	1 626 s	1 675 m	1 624 s	1 679 m
19	1 619 s	1 661 s	1 608 s	1 662 s
20	1 605 s	1 625 s	1 604 s	1 628 s
21	1 606 vw	1 668 s	1 604 w	1 673 w
22	1 594 vw	1 662 s	1 601 vw	1 661 m
23	1 598 w	1 621 s	1 608 w	1 611 m
24	1 632 s	1 684 m	1 621 s	1 687 w
25	1 610 s	1 671 s	1 617 s	1 675 m
26	1 604 s	1 647 s	1 605 w	1 648 w

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