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ABSORPTION AND FLUORESCENCE SPECTRA OF 7-AMINOCOUMARIN DERIVATIVES

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Summary

The absorption and fluorescence spectra of twelve 7-aminocoumarin derivatives have been studied with methanol and chloroform as solvents. Electronic transitions to $n\pi^*$ states have been traced. The effect of different substituents on the nitrogen was easily observed in the fluorescence spectra. Fluorescence quantum yields and oscillator strengths were evaluated. The role of hydrogen bonding on emission maxima, quantum yields and photolytic dissociation were discussed.

1. Introduction

One of the most notable physical properties of most of the coumarin derivatives is their excellent fluorescence. The efficient fluorescing nature of the coumarins has been effectively exploited in their use as optical brightening agents in detergents, papers and textiles [1], in dye laser techniques [2, 3] and as proposed units for photobiological energy transfer processes. Coumarin crystals are monoclinic [4]. Peck observed that organic compounds that have a molecular symmetry equivalent to or higher than C_s can act as dye lasers [5] on dissolution in an organic solvent which has output in the blue region of the spectrum. A qualitative comparison of the effect of the composition of the coumarin on the intensity of the UV absorption and fluorescence spectra was made by Balaiah *et al.* [6]. Wheelock [7] and Crosby and Berthold [8] observed that the effects of substitution and the solvent can be more readily detected by fluorescence spectra than by electronic absorption spectra. Fink and Koehler [9] provided data on the changes in emission spectra of umbelliferone as a function of pH, solvent and excitation wavelength in aqueous media. Attempts have been made to discover the relationship between fluorescence and structure, and it was found that the Taft resonance and inductive electron withdrawing parameters do not correlate well with fluorescence intensity [10].

Owing to the immense practical value of coumarins as optical brightening agents, we have undertaken an extended study of the absorption and

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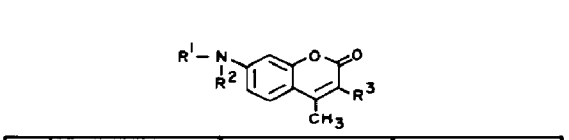

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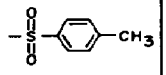
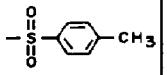
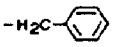
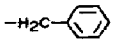
3		H	H
4			H
5		H	H
6			H
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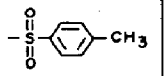
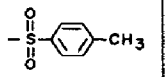
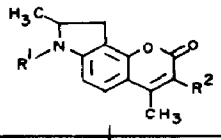
8		H	
9			



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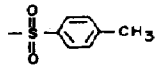
10		H
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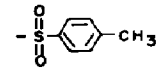
12		

Fig. 1. Structures of the coumarin derivatives investigated.

emission properties of some of the new coumarin derivatives prepared in our laboratory and in this paper report the fluorescence quantum yields ϕ, oscillator strengths f and low frequency half-value components n_H (see Section 3.2) of the compounds (defined in Fig. 1) in methanol and chloroform.

2. Experimental details

The coumarin derivatives were synthesized as described in ref. 11 and the microanalytical data are presented in Table 1. All the compounds were purified either by means of column chromatography or recrystallization. Methanol, isopropanol, butanol, chloroform, dichloromethane and dichloroethane were purified by standard procedures. The electronic absorption spectra were recorded by employing a Specord UV–visible spectrophotometer. Fluoroescence spectra were recorded using an Aminco–Bowman spectrofluorometer (J_4-8960 model with a J_{10} 222A microphotometer). The widths of the emission entrance slit and excitation exit slit were kept constant throughout the measurements. Relative fluorescence quantum yields were obtained by means of the optically dilute measurement technique using the Parker–Rees [12] relationship without a refractive index correction. The fluorescence standard used was quinine sulphate dihydrate (Loba

TABLE 1

Microanalytical and IR spectral data for 7-aminocoumarin derivatives

Serial number	*Molecular formula*	*Melting point*[a] (°C)	*Microanalysis*[b]			*IR spectrum (KBr)* (cm^{-1})	
			C	*H*	*N*	*>C=O*	*>N—H*
1	$C_{10}H_9NO_2$	222	68.5 (68.5)	5.1 (5.2)	7.9 (8.0)	1700	3350 3430
2	$C_{13}H_{13}NO_2$	110	72.5 (72.5)	6.0 (6.1)	6.5 (6.5)	1695	3330
3	$C_{17}H_{15}NO_4S$	210	61.8 (61.9)	4.5 (4.6)	4.2 (4.6)	1690	3150
4	$C_{20}H_{19}NO_4S$	108	64.9 (65.0)	5.2 (5.2)	3.8 (3.8)	1740	—
5	$C_{17}H_{15}NO_2$	103	76.9 (76.9)	5.6 (5.7)	5.2 (5.3)	1695	3310
6	$C_{20}H_{19}NO_2$	133	78.6 (78.6)	6.3 (6.3)	4.6 (4.6)	1730	—
7	$C_{16}H_{13}NO_2$	280	76.3 (76.5)	5.1 (5.2)	5.5 (5.6)	1670	3345 3450
8	$C_{23}H_{19}NO_4S$	242	68.1 (68.1)	4.7 (4.7)	3.4 (3.5)	1670	3200
9	$C_{26}H_{23}NO_4S$	136	70.1 (70.1)	5.2 (5.2)	3.2 (3.2)	1700	—
10	$C_{20}H_{19}NO_4S$	165	65.0 (65.0)	5.2 (5.2)	3.7 (3.8)	1725	—
11	$C_{13}H_{13}NO_2$	137	72.5 (72.5)	6.1 (6.1)	6.5 (6.5)	1690	3310
12	$C_{26}H_{23}NO_4S$	123	70.0 (70.1)	5.2 (5.2)	3.1 (3.1)	1700	—

The values in brackets are calculated.

[a]Uncorrected.

[b]Microanalyses were in satisfactory agreement with calculated values: C, ±0.05; H, ±0.05; N, ±0.05.

Chemi; molecular weight, 782.97). This was recrystallized twice from a 50vol.%ethanol–50vol.%water mixture and the solutions were prepared in 0.1 N H_2SO_4 (molar absorptivity measured at 345 nm: absorption maximum, 5.02×10^3 dm^3 mol^{-1} cm^{-1}). We used the same experimental condi-

tions as Melhuish [13] while employing quinine sulphate for fluorescence measurements. Aerated stock solutions were freshly prepared on the day of measurement, and the temperature was kept at 23 ± 1 °C. The uncertainty in ϕ, f and n_H is ±3%.

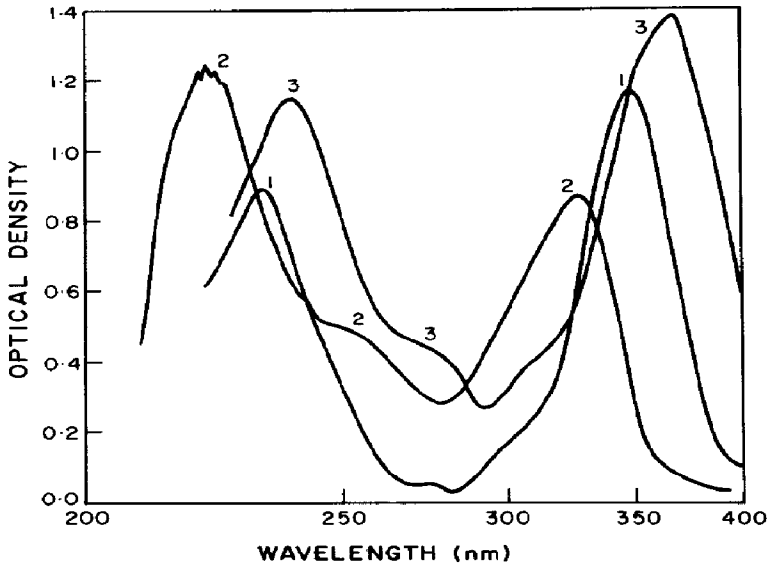


Fig. 2. Absorption spectra: curves 1, 2 and 3 correspond to compounds 1 (6.9×10^{-5} mol dm^{-3}), 10 (5.56×10^{-5} mol dm^{-3}) and 11 (8.9×10^{-5} mol dm^{-3}) respectively in methanol.

3. Results and discussion

3.1. Electronic absorption spectra

Substitution at the nitrogen of 7-amino-4-methylcoumarin markedly alters the absorption spectrum of the compound (1). The electronic absorption spectra of **1**, **10** and **11** are shown in Fig. 2 and the spectroscopic data for the compounds studied are presented in Tables 2 and 3. It is seen from Table 2 that most of the compounds exhibit two intense absorption bands at 237 ± 7 nm, 354 ± 13 nm and a weak band at 294 ± 8 nm. Invariably they also show two characteristic minima, one around 265 nm and the other at 300 nm. The theoretical Hückel molecular orbital approach has been applied to the study of absorption spectra of substituted coumarins and it has satisfactorily been shown that the absorptions are due to π–π^* transitions [15 - 17]. In our compounds also the high intensity bands at 237 and 354 nm could be assigned to π–π^* transitions, but the third low intensity shoulder at 294 nm has a low molar extinction coefficient and is sensitive to solvents in which hydrogen bonding occurs. A close examination of Tables 2 and 3 reveals that with methanol as the solvent the shoulder was

TABLE 2

Spectroscopic data for 7-aminocoumarin derivatives in methanol

Serial number	λ_{max} (nm)	ϵ ($dm^3\ mol^{-1}\ cm^{-1}$)	f	λ_{flu} (nm)	ϕ	n_H[a] (cm^{-1})	n_H(exp) (cm^{-1})
1	231	12783	0.30	439	0.33	2383	1872
	271	667					
	293	2667					
	348	16812					
2	237	14786	0.36	448	0.38	2030	1530
	293	5286					
	365	19898					
3	232	16324	0.40	443	0.39	2565	2043
	292	4186					
	345	17938					
4	218	17927	0.16	415,430	—	3100	2043
	280	8403					
	344	8403					
5	240	11921	0.31	441	0.77	1919	1536
	310	4966					
	364	16391					
6	241	13044	0.36	440	0.79	1898	2095
	310	3727					
	364	21118					
7	240	12258	0.38	446	0.15	2299	1823
	355	23871					
8	235	11877	0.37	456	0.12	2923	2155
	294	6482					
	342	18519					
9	235	20290	0.36	434,439	—	3283	2386
	294	16232					
	320	20281					
10	219	22302	0.38	423,467,477[b]	—	2814	2108
	250	8813					
	326	15648					
11	238	11015	0.26	479	0.58	2548	2184
	270	4310					
	367	13295					
12	235	19380	0.45	428,469	—	2849	2245
	250	14923					
	328	21512					

[a]Estimated according to the rule given in ref. 14.
[b]In 30vol.%HNO_3–70vol.%methanol.

TABLE 3

Spectroscopic data for 7-aminocoumarin derivatives in chloroform

Serial number	λ_{max} (nm)	ϵ ($dm^3\ mol^{-1}\ cm^{-1}$)	f	λ_{flu} (nm)	ϕ	n_H[a] (cm^{-1})	n_H(exp) (cm^{-1})
1	333	13497	0.17	406	0.39	2160	1831
2	310	4769	0.19	415	0.44	1950	2318
	345	18480					
3	294	6655	0.36	406	0.48	2196	1819
	332	21160					
4	285	9445	0.23	406	0.41	2726	2053
	318	12100					
5	310	3230	0.35	425	0.81	1856	1648
	355	12380					
6	313	1930	0.25	425	0.94	1669	1034
	361	16984					
7	339	15992	0.27	431	0.22	2519	1937
8	297	7159	0.40	428	0.18	3038	2104
	323	20048					
9	295	9876	0.31	424	0.20	2950	2532
	323	15741					
10	328	20455	0.39	432	0.49	2935	1851
11	261	3581	0.28	422	0.62	2355	3412
	325	12633					
	338	15957					
12	256	8159	0.36	422	0.25	2642	2729
	330	17364					

[a]Estimated according to the equation given in ref. 14.

blue shifted by approximately 10 nm. A detailed study of 2 in various solvents showed that in isopropanol and *n*-butanol the shoulder appeared at 295 nm while in dichloromethane and dichloroethane it appeared at 310 nm. Based on the above results the shoulder at 294 nm may presumably be attributed to an $n\pi^*$ transition arising from the lone pair electrons of the benzopyran ring.

The effect of solvents on the low frequency $\pi-\pi^*$ transition is as expected. In methanol this absorption maximum appeared at 354 ± 13 nm while in chloroform it appeared at 342 ± 20 nm. This can be explained as methanol is a proton donating solvent which can form hydrogen bonds and thereby shifts the transition to longer wavelengths. As can be seen from Table 3, substitution on the nitrogen of 7-amino-4-methylcoumarin has

a pronounced effect on the absorption wavelength. It was noticed that when the primary amino group was modified to tertiary by the use of substituents such as allyl or benzyl, a red shift of 12 - 28 nm occurred, possibly owing to the increase in the normal movement of charge from the 7-amino group to the pyrone carbonyl group. But compounds **4**, **9**, **10** and **12** constitute another set, which exhibit absorption at shorter wavelengths. In order to examine further whether the 345 nm band is due to a forbidden transition as was proposed by Matoo [18], the oscillator strength f, which is a measure of energy and intensity, has been evaluated. The oscillator strength of the 345 nm band was estimated using the equation

$$f \approx 4.32 \times 10^{-9} \epsilon_{max} \Delta\nu_{1/2}$$

where ϵ_{max} is the molar absorption coefficient at the maximum of the 345 nm band and $\Delta\nu_{1/2}$ is the width in reciprocal centimetres of the band between the two frequencies at which $\epsilon = (\frac{1}{2})\epsilon_{max}$. The values are presented in Tables 2 and 3. They are large, solvent dependent and vary from 0.15 to 0.45 which suggest that the electronic transition is not forbidden.

3.2. Fluorescence spectra

As the fluorescence intensities of coumarin solutions vary irregularly at higher concentrations and in order to minimize the re-absorption effects, the solutions for the fluorescence quantum yield measurements were prepared in such a way that the optical density was generally kept below 0.05 for a path length of 1 cm. In Fig. 3 the linearity of the plot of fluorescence intensity against (extremely low) concentration of compound **11** is shown. All the compounds were excited at their respective absorption maxima (345 nm band). The shape and emission maxima are independent of the exciting wavelength between 330 and 380 nm.

All the compounds exhibited an intense blue and blue–green fluorescence in methanol as well as in chloroform. These bands are assigned to normal $\pi^* \rightarrow \pi$ fluorescence analogous to the absorption; the fluorescence of the coumarins has also been traced to the α,β-unsaturated lactone carbonyl group conjugated with the benzene ring [16]. Substituents have more influence on fluorescence maxima than on absorption maxima. 4-Methylcoumarin gives a fluorescence maximum at 383 nm [7]. A large bathochromic shift of 56 nm is seen in changing from 4-methylcoumarin to 7-amino-4-methylcoumarin. Similar shifts of 40 nm are also seen between **1** and **11**. When a phenyl group is substituted at the 3-position, there is a possibility of extensive delocalization of π electrons, causing the fluorescence maxima to red shift. It is clear that insertion of allyl, benzyl and tosyl groups on the nitrogen of 7-amino-4-methylcoumarin and the pyrrole ring fused at the 7- and 8-positions shifts the fluorescence maxima to longer wavelengths. The shifts in methanol are much higher than those in chloroform. The fluorescence spectra of these compounds show a greater wavelength dependence on the solvent polarity than do the absorption spectra, which suggests that the excited state is more polar than the ground state.

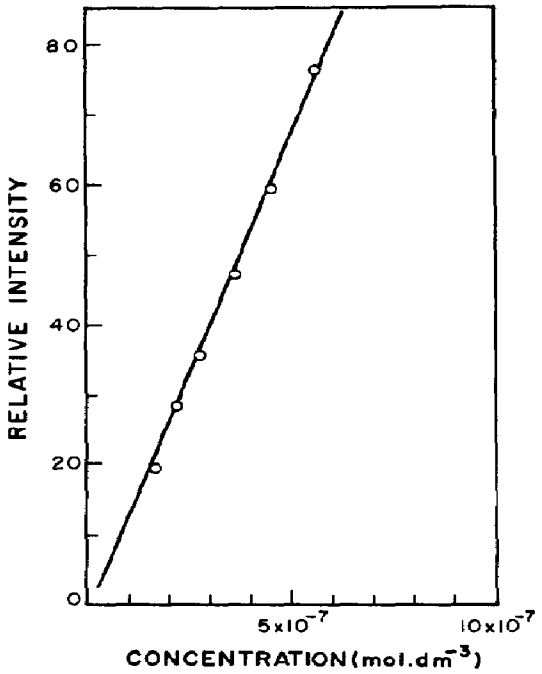


Fig. 3. Linearity of fluorescence intensity of 11 *vs.* concentration in methanol.

Tables 2 and 3 reveal that the fluorescence quantum efficiency of all the compounds investigated is higher in chloroform. The possible reason for low quantum efficiency in methanol is that a non-radiative degradation of the excited state takes place owing to the delocalization of π electrons through hydrogen bonding [19]. The quantum yields are high and range from 0.12 to 0.79 in methanol and from 0.18 to 0.94 in chloroform.

Substitution of the phenyl ring of 7-amino-4-methylcoumarin at the 3-position does not produce a substantial change in the fluorescence intensity whereas benzyl and allyl groups on the nitrogen have a remarkable effect. Compounds 5 and 6 show re-absorption effects even at a concentration of 5.6×10^{-6} mol dm^{-3}, while below 1.8×10^{-6} mol dm^{-3} compound 6 gave a constant value of 0.94 ± 0.015 for the quantum yield.

It was observed from their absorption spectra that compounds 4, 9, 10 and 12 are somewhat different from the rest, and similarly they exhibit two different types of unusual behaviour under the influence of light in two different solvents. When the amino group of 7-amino-4-methylcoumarin is secondary, it emits at a longer wavelength with increased quantum efficiency, and the tertiary amine likewise has a higher efficiency than the secondary amine. But 4, 9, 10 and 12 are not stable in methanol under the influence of light (330 - 380 nm). The effect of irradiation of compound 10 for various lengths of time is shown in Fig. 4. Similar spectra were also recorded for 4, 9 and 12. The spectral curves show a decrease in intensity of the 423 nm band of 10 and an increase in the intensity at 467 nm with

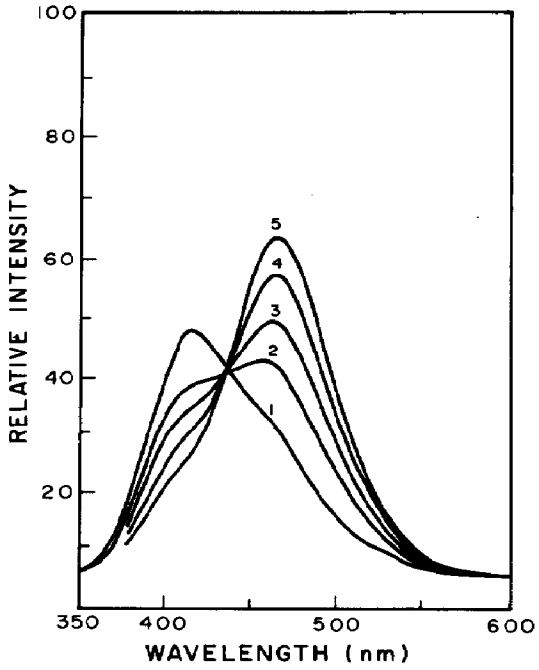


Fig. 4. Fluorescence spectra of 10 in methanol: curves 1 - 5 correspond to the spectral curves after 0, 5, 10, 15 and 20 min in the light path.

time giving an isosbestic point at 437 nm. The presence of an isosbestic point indicates the existence of a photolysed product and an unphotolysed compound. This is further confirmed by more than two spots appearing in the thin-layer chromatography of the irradiated sample while the unirradiated sample gave only one spot. The characteristic emission spectrum of the irradiated solution was obtained even after keeping it in darkness for 1 day. The absence of the unusual behaviour of these compounds in chloroform indicates a specific interaction between **4**, **9**, **10** and **12** and methanol.

It appears that this specific interaction may be the solvolysis of the sulphonamide group. The reasoning here follows from the assumption that the hydroxyl proton of methanol forms a hydrogen bond with the tightly bound electrons of the oxygen of the tosyl group, resulting in enhanced solvation of sulphonic oxygens in their ground state; this would tend to polarize the bond between sulphur and nitrogen thereby providing a basis for photodissociation under the influence of light. It is well known that alkyl and aryl sulphones undergo solvolysis in water [20]. In alkaline media, coumarin and substituted coumarins are labile and there were several changes in their spectra, while they remain stable in acidic media [7, 8]. Interestingly, when compound **10** (3.65×10^{-6} mol dm^{-3} in 30vol.%HNO_3–70vol.%-methanol) was kept in the light path for 10 min its emission spectrum almost superimposed on that of detosylated **11** (Table 2 and Fig. 5). Furthermore, a TLC comparison of the photolysed product with compound **11** revealed

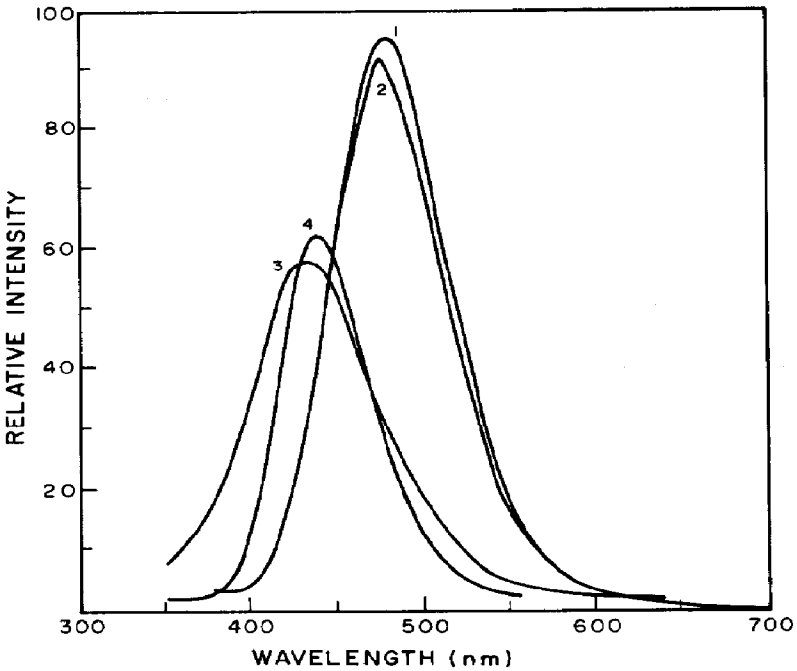


Fig. 5. Fluorescence spectra: curve 1, 11 in methanol; curve 2, 10 in 30vol.%HNO_3–70vol.%methanol; curve 3, 10 in chloroform; curve 4, 3 in methanol.

identical R_f values. These results indicate that the photochemical changes that take place under the influence of light may be due to a detosylation reaction. Typical cleavages at the nitrogen of 7-aminocoumarin derivatives have already been reported in the case of 7-diethylamino-4-methylcoumarin [21, 22].

As the coumarin derivatives are ideal optical brighteners, an attempt has been made to find out the relationship between the shape of the absorption band and the fluorescence maximum with the aid of the Pestemer rule [14]:

$$\Delta = 2.5 n_H$$

where Δ is the distance between the absorption and emission maxima and n_H is the low frequency half-value component. The difference between the wavenumber of the maximum of the absorption curve and the wavenumber of the half-height of its low frequency branch was designated the low frequency half-value component. The Pestemer rule is illustrated in Fig. 6. In the last two columns of Tables 2 and 3, the calculated and experimental n_H values are presented. The values are encouraging but largely dependent on the medium used. It was observed that the experimental values were not in accordance with those calculated and therefore deviate from the rule. It is understandable that the rule is not obeyed in these cases; this is presumably because it does not take the solute–solvent interaction into consideration.

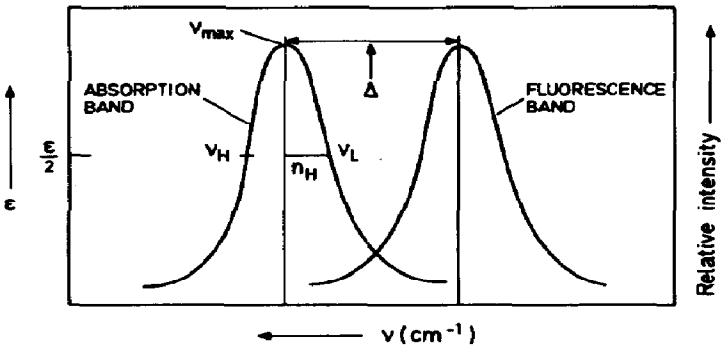


Fig. 6. Illustration of the Pestemer rule.

The results obtained from the above studies indicate that the closely spaced $n\pi^*$ and $\pi\pi^*$ electronic transitions can be traced by either changing the solvent or the substituent. 7-Aminocoumarin is a potential source of fluorescence and its derivatives are promising fluorescence brightening agents as they absorb around 340 - 370 nm and emit between 405 and 480 nm with a high quantum efficiency.

Acknowledgments

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