

761. *The Luminescence of Some Substituted Naphthalenes.*

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The luminescence spectra of the fourteen isomeric nitronaphthylamines and ten isomeric dinitronaphthalenes have been measured at low temperatures. A new form of electronic phosphorometer was used. The emission from the nitronaphthylamines for all except three compounds was found to be fluorescence, and in all cases luminescence was weak. Comparison of fluorescent and phosphorescent maxima with absorption maxima suggests that the first excited singlet and triplet levels have similar energies. In the spectra of the dinitronaphthalenes a wide separation was found between the first two bands, the usual interval being approximately 1400 cm^{-1} . Probable assignments are suggested for the bands found in these spectra.

THE emission spectra of a number of aromatic nitro-amines in rigid media at low temperatures have been described.¹ We have now investigated the emission spectra of the fourteen nitronaphthylamines and the ten dinitronaphthalenes under similar conditions,

¹ Foster, Hammick, Hood, and Sanders, *J.*, 1956, 4865.

using an electronic phosphorometer of increased sensitivity and stability. The principle of this phosphorometer is that the photomultiplier used to measure the luminescence is switched off during the periods when the specimen is being illuminated.

EXPERIMENTAL

The cooling apparatus was that described by Bowen and Brocklehurst² for the measurement of luminescence spectra at low temperatures. The emission from the frozen samples was passed through a Hilger constant-deviation spectrometer with an E.M.I. photomultiplier at the exit slit. The emission was excited by the filtered radiation (3650 Å) from a mercury arc lamp which was energised through a heavy-duty half-wave rectifier connected to the 50 cycles/sec. mains A.C. supply. The lamp arc was thus struck and the sample illuminated for only half of each mains cycle, leaving the other half available for the recording of phosphorescence. A pulse generator which was phase locked to the mains was connected to the photomultiplier so that pulses of such polarity as to reverse the potential drop could be applied to the sixth and seventh dynodes. By adjusting the width and phase of these blocking pulses the photomultiplier could be effectively switched off during the half cycles when the mercury arc was struck and the sample illuminated. The photoelectric current was measured by means of a Tinsley galvanometer. Fluorescence spectra could be measured either by shifting the pulse phase by 180° or by switching the generator off.

The spectrometer-photocell combination was calibrated for quantum sensitivity by measuring the photocurrent at various wavelengths when a B.T.H. standard filament lamp was used as a light source. Measured spectra could be then converted to a relative quantum-wave number basis. It was found that the calibration curve was not affected by the pulse generator operation. By interposing filters of known transmittance between the source and the spectrometer slit, the photocurrent was found to be directly proportional to the light falling on the cell during calibration.

The Measurement of Emission Spectra.—When measuring emission spectra the usual procedure was to scan through the spectrum (4000—6000 Å) without the pulse generator and then to repeat the scan with the generator switched on to detect phosphorescence. For relatively long-lived phosphors, since the phosphorescence readings involved only the half-cycles when the lamp was off, the signal was halved by the use of the pulse generator. Phosphorescence in the presence of simultaneous fluorescence was determined by subtracting twice the observed phosphorescence signal from the total (generator off) signal. In the case of pure phosphorescence an estimate of the lifetime could be made from the signal ratios obtained with and without the generator.

The blocking of fluorescent radiation by the pulse generator technique is extremely efficient; thus for an anthracene sample the signal with the generator switched on was about 1/250 of the signal with the pulses off. The period between the cessation of specimen excitation and the observation of the emission is also short (1 msec.) and thus phosphorescence with a half life of down to 3 msec. can be measured. In the present work, the spectral maxima positions were reproducible to ± 15 cm.⁻¹.

The Measurement of Absorption Spectra.—Absorption spectra were measured with a Unicam SP 500 instrument.

Preparation of Materials.—The naphthalene compounds were prepared by standard procedures and after chromatography were recrystallised until both the emission spectra and the m. p. were constant. The preparation of the 2,3-substituted derivatives afforded some difficulty, the methods of Ward and Coulson⁴ being finally adopted.

Solvents.—(a) *Methanol.* The blue luminescence of the commercial alcohol was removed by fractional distillation over sodium hydroxide.

(b) *Ethanol.* The "spectroscopic" grade alcohol used has a faint blue fluorescence when frozen. This luminescence was substantially reduced by treatment with magnesium turnings (Grignard grade), followed by fractional distillation.

(c) *Ethylene glycol.* B.D.H. glycol when freshly distilled under reduced pressure showed no luminescence on freezing.

(d) *Ethyl iodide.* This compound was purified by the method given by Vogel, "Textbook of Practical Organic Chemistry," 3rd edn., Longmans, Green and Co. Ltd., London, 1957, p. 287.

² Bowen and Brocklehurst, *J.*, 1954, 3875.

RESULTS

The Nitronaphthylamine Spectra.—The emissions from glycol–alcohol glasses (4 : 1 v/v) had the same band-shapes as those from the more usual ethanol–methanol glasses, but were much more intense, presumably owing to the higher viscosity of the former solvent. The photoelectric determinations were therefore made by using the glycol solvent and the results are given in Table 1. The results marked with an asterisk are the extrapolated short-wave limits of the emissions; in these cases the maxima lay beyond the sensitive range of the apparatus. The Table also gives the separation between the lowest absorption band and the emission-band maxima ($\Delta\nu$).

TABLE 1.

Compound	Emission maxima (cm. ⁻¹)	$\Delta\nu$ (cm. ⁻¹)	Process †	Compound	Emission maxima (cm. ⁻¹)	$\Delta\nu$ (cm. ⁻¹)	Process †
1-Naphthylamines				2-Naphthylamines			
2-nitro-	18,300	5200	F	1-nitro-	17,350	6650	P
3-nitro-	17,150	6950	F	3-nitro-	19,500 *	—	F
4-nitro-	17,400	6000	P	4-nitro-	17,150	7300	F
5-nitro-	17,100	7000	P	5-nitro-	17,050	—	F
6-nitro-	20,100 *	—	F	6-nitro-	19,400	5400	F
7-nitro-	18,900 *	—	F	7-nitro-	17,250	7450	F
8-nitro-	17,300	6200	F	8-nitro-	17,400	6400	F

† F = fluorescence. P = phosphorescence.

TABLE 2.

Dinitro-naphthalenes	Total luminescence (cm. ⁻¹)	Emission-band separations (cm. ⁻¹)	Phosphorescence (cm. ⁻¹)	Dinitro-naphthalenes	Total luminescence (cm. ⁻¹)	Emission-band separations (cm. ⁻¹)	Phosphorescence (cm. ⁻¹)
1,2- †	17,300	—	17,300	1,6-	19,600	0	19,650
1,3-	19,230	0	19,230	1,6-	18,200	1400	18,200
	17,800	1430	17,800		16,950	2650	16,900
	16,600 *	2630 *	—	1,7-	19,150	0	19,200
1,4-	17,850	0	17,800	1,7-	17,750	1400	17,725
	16,400	1450	—	1,8-	19,900	0	19,900
1,5-	19,125	0	19,125	1,8-	18,450	1450	18,500
	17,700	1425	17,650		17,150	2750	17,150
	16,400 *	2725 *	—	2,3- †	18,300	—	18,350
1-Nitronaphthalene {	18,800	0	18,800	2,6-	18,850	0	18,850
alene {	17,400	1400	17,400	2,6-	17,350	1500	17,350
2-Nitronaphthalene {	19,550	0	19,550	2,7-	19,450	0	19,450
alene {	18,150	1400	18,150	2,7-	18,050	1400	18,100

* Measurements approximate. † No clear structure.

The emission spectra of these compounds were also photographed to see if any other bands were present in the region 6000–7000 Å (where the photomultiplier was insensitive). These determinations showed only a single band at the same wavelength as that found photoelectrically.

The Nitronaphthalenes.—The emission maxima of these compounds in the frozen alcohol mixtures are given in Table 2. The wide separation of the first two bands (1400 cm.⁻¹) in the majority of these spectra suggested that processes other than simple β -phosphorescence might be occurring. The relative intensities of the bands were therefore examined both as a function of temperature and in the presence of ethyl iodide.³ Despite variations in intensities of a factor of ten in these experiments the relative intensities remained unaltered.

DISCUSSION

The Nitronaphthylamines.—The lowest-energy transition in the nitronaphthylamines probably arises in the excitation of one of the lone pair electrons of the amino-group to

³ Graham-Bryce and Corkill, *Nature*, 1960, **186**, 965.

⁴ Ward and Coulson, *J.*, 1954, 4545.

give a state of the (n, π^*) type. It has been shown by Reid⁵ that such states show much smaller splitting between the singlet and triplet levels than the (π, π^*) type. The frequency differences between the absorption and emission bands of these compounds (Table 1) are of the same order whether the process is phosphorescence or fluorescence; as the first excited singlet (F) level might be expected to lie in the same relative position between the absorption and fluorescence bands in all these compounds, it appears that the singlet and triplet levels are very close. The absence of vibrational structure in the emission spectra is not unexpected as the $^3(n, \pi^*)$ excited state is highly polar and so considerable solvent interaction would be likely.

The occurrence of phosphorescence in only three of these compounds is surprising as Kasha⁶ has pointed out that (n, π^*) states have large spin-orbit interactions which will facilitate transfer from higher singlet states into the $^3(n, \pi^*)$ phosphorescence level. The luminescences of these compounds are all weak and it would seem probable that quenching of the triplet level by solvent or impurity interaction is responsible for the absence of phosphorescence rather than inefficient transfer from the singlet state. The solutions were not degassed, so that dissolved oxygen would be a possible quenching agent even at the high viscosities of the frozen solvents used.

The Nitronaphthalenes.—The temperature independence of the intensity ratios of the bands of these compounds shows that the two bands do not correspond to the presence of both α - and β -phosphorescence processes.⁷ The effect of adding ethyl iodide to the alcohol solvent (2 : 3 v/v) was to increase the intensity of the emissions and to decrease the half-lives of the phosphorescences,³ but to leave the relative intensities unaltered. Since dilution and long exposure to unfiltered ultraviolet light were also without effect on the shapes of the spectral curves, the experimental results are inconsistent with processes other than transitions from the triplet level to various vibrational modes of the ground state.

The selection rules governing the appearance of various vibrational modes in a spectrum are related to the elements of symmetry of the vibrations themselves and the electronic distributions of the two states between which the transition occurs. For an orbitally permitted transition in which the two electronic states belong to the same point group the permitted vibrational modes belong to the totally symmetrical representation of the group. The phosphorescence transition for naphthalene itself is orbitally permitted,⁸ and Sidman⁹ found that for the halogenonaphthalenes the most prominent vibrations could be related to the totally symmetrical (A_g) motions of naphthalene. He concluded that these molecules possessed the same elements of symmetry in the ground and triplet levels.

The first band for these compounds may be assigned to the 0-0 transition, the interval to the second band in most of these compounds (1400 cm^{-1}) corresponding to an A_g mode in which the C-C bond common to both rings (the 9,10 bond) is stretched.¹⁰ In some of these spectra a third band at $2700\text{--}2750\text{ cm}^{-1}$ from the 0-0 band could be detected; a probable assignment for this band is to a combination of a B_{1g} (forbidden) vibration with another A_g mode ($A_g + B_{1g} = 2730\text{ cm}^{-1}$). The appearance of this B_{1g} mode in the phosphorescence spectra of other disubstituted naphthalenes both alone and in combination led Ferguson *et al.*¹¹ to suggest that the triplet state belonged to a lower symmetry point group than the ground state.

In the dinitronaphthalenes the only fundamental appears to be the 1400 cm^{-1} A_g mode. As the B_{1g} vibration occurs only as a combination with another A_g mode and as the same vibrational pattern is observed with isomers of widely differing symmetry, it seems that

⁵ Reid, *J. Chem. Phys.*, 1953, **21**, 1906.

⁶ Kasha, *Discuss. Faraday Soc.*, 1950, **9**, 14.

⁷ Lewis, Lipkin, and Magel, *J. Amer. Chem. Soc.*, 1941, **63**, 3005.

⁸ Craig, *Proc. Int. Congr. Pure Appl. Chem.*, 1947, **11**, 411.

⁹ Sidman, *J. Chem. Phys.*, 1956, **25**, 229.

¹⁰ Lippincott and O'Reilly, *J. Chem. Phys.*, 1955, **23**, 238.

¹¹ Ferguson, Iredale, and Taylor, *J.*, 1954, 3160.

the distortion of the triplet state and the perturbation of the π orbitals by the nitro-groups must be small. Since the triplet state belongs to the $^3(\pi, \pi^*)$ type the solvent interaction so prominent in the amino-compounds is absent and relatively sharp spectra are obtained. The intensities of the three bands found in these spectra are of the same order. Since the 1400 cm.^{-1} mode is prominent in almost all cases it is possible that the triplet state in these compounds is only slightly distorted by an expansion of the 9,10 bond relative to the ground state. Since in the ground state this bond shows the greatest degree of fixation, its expansion when electrons are unpaired to form the triplet state might be expected.

When the two substituent groups are adjacent to each other (as in the 1,2- and 2,3-isomers) the vibrational structure was no longer found and diffuse bands only were obtained. This effect may be interpreted as due to steric hindrance between the nitro-groups resulting in skeletal distortion of the molecule and a breaking down of the selection rules.

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