1043. *Excimer Fluorescence of Some Naphthalene Derivatives in the Molten State.*

By B. Stevens and T. Dickinson.

The fluorescence spectra of 1- and 2-fluoro- and 1- and 2-methyl-naphthalene in the liquid state have been recorded. Both molecular and excimer fluorescence bands, identified from the concentration- and temperature-dependent fluorescence spectra of the dissolved compounds, are emitted by the pure liquids, the ratio of molecular to excimer band intensities increasing with temperature.

The absence of excimer self-quenching is discussed and it is suggested that the failure to detect fluorescence from other molten aromatic compounds is a consequence of the relatively high temperatures required rather than of the high molecular concentration.

Although aromatic hydrocarbons and their derivatives constitute a major class of fluorescent molecules,[1] the extent to which their fluorescence is observed depends on the molecular environment. In fluid media in the absence of foreign quenching species, the quantum yield γ_M of molecular fluorescence is given by

$$\gamma_M = k_1/(k_1 + k_2 + k_3[A]), \qquad (I)$$

where the rate constants refer to the processes (1), (2), and (3) of radiative relaxation, intersystem crossing (or internal deactivation), and collisional quenching by an unexcited molecule A of the same species, respectively:

$$A^* \longrightarrow A + h\nu' \qquad (1)$$

$$A^* \longrightarrow {}^3A \text{ (or A)} \qquad (2)$$

$$A^* + A \longrightarrow \text{Quenching} \qquad (3)$$

Thus, since the quantum yield often approaches zero at high concentrations,[2,3] molecular fluorescence is observed only in dilute solutions or in the gas phase at lower pressures.

Despite the high molecular density of the crystalline form, these compounds are often fluorescent in the solid state[4] where the interaction of excited and unexcited molecules at adjacent lattice sites is severely limited by their separation and relative orientation. If, however, these restrictions are removed, self-quenching should be dominant at these concentrations and the fluorescence yield virtually zero; this explanation usually accompanies statements[5] to the effect that molecules of this class are non-fluorescent in the molten state.

Recent observations[6,7] have shown that, although the molecular fluorescence of a planar aromatic hydrocarbon is quenched as its concentration in solution is increased, this is often replaced by a broad, structureless emission band at longer wavelengths originating in the radiative relaxation of the excimer A_2^* (process 5) produced by photoassociation (process 4):

$$A^* + A \longrightarrow A_2^* \qquad (4)$$

$$A_2^* \longrightarrow 2A + h\nu'' \qquad (5)$$

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[1] Bowen, *Quart. Rev.*, 1947, **1**, 1.

[2] Melhuish, *J. Phys. Chem.*, 1961, **65**, 229.

[3] Klerk, *Mol. Phys.*, 1958, **1**, 141.

[4] *E.g.*, Sangster and Irvine, *J. Chem. Phys.*, 1956, **24**, 670; Northrop and Simpson, *Proc. Roy. Soc.*, 1956, *A*, **234**, 136; Birks and Cameron, *ibid.*, 1959, *A*, **249**, 297; Stevens, *Spectrochim. Acta*, 1962, **18**, 439.

[5] *E.g.*, Pringsheim, "Fluorescence and Phosphorescence," Interscience Publ., Inc., New York, 1949, p. 285.

[6] Forster and Kasper, *Z. Elektrochem.*, 1955, **59**, 977.

[7] Birks and Christophorou, *Nature*, 1962, **196**, 33; 1963, **197**, 1064; *Spectrochim. Acta*, 1963, **19**, 401.

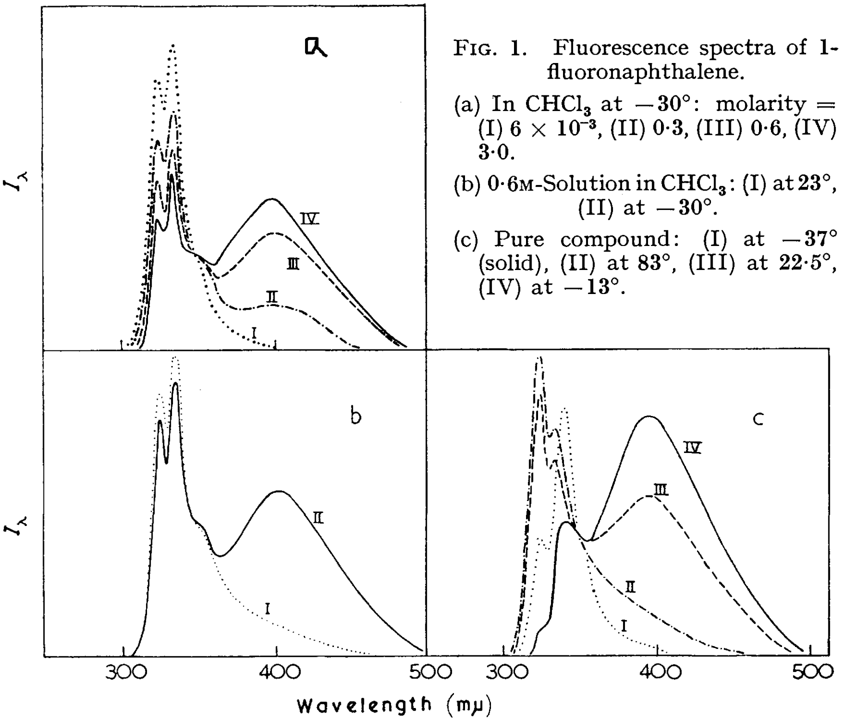

FIG. 1. Fluorescence spectra of 1-fluoronaphthalene.

(a) In $CHCl_3$ at −30°: molarity = (I) 6 × 10^{-3}, (II) 0·3, (III) 0·6, (IV) 3·0.

(b) 0·6M-Solution in $CHCl_3$: (I) at 23°, (II) at −30°.

(c) Pure compound: (I) at −37° (solid), (II) at 83°, (III) at 22·5°, (IV) at −13°.

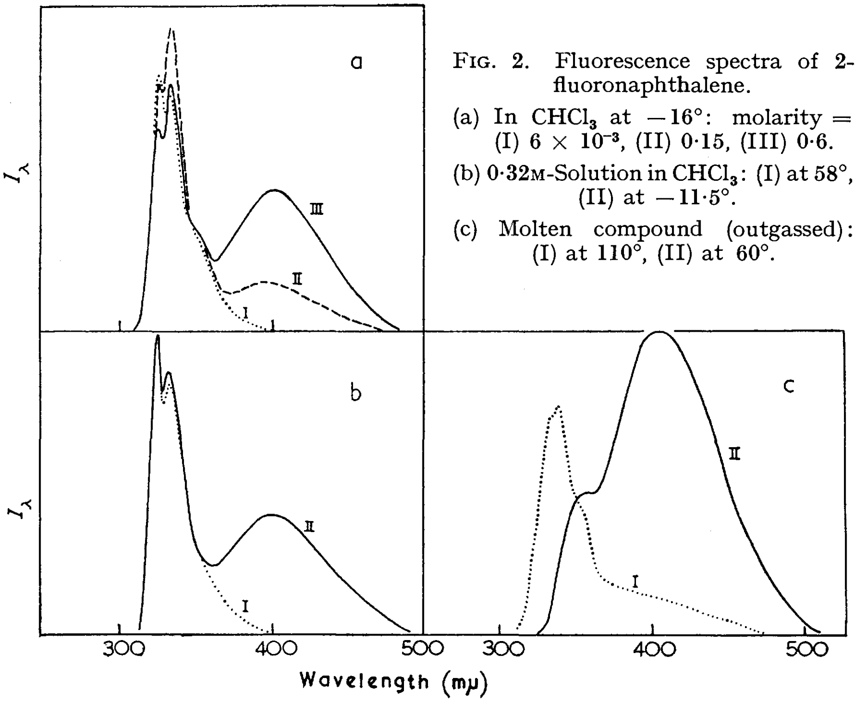

FIG. 2. Fluorescence spectra of 2-fluoronaphthalene.

(a) In $CHCl_3$ at −16°: molarity = (I) 6 × 10^{-3}, (II) 0·15, (III) 0·6.

(b) 0·32M-Solution in $CHCl_3$: (I) at 58°, (II) at −11·5°.

(c) Molten compound (outgassed): (I) at 110°, (II) at 60°.

This emission, in turn, is subject to competition from radiationless relaxation (process 6) which may involve permanent dimerisation, together with dissociation (process 7) which requires an activation energy of some 6—10 kcal./mole:[8,9]

$$A_2^* \longrightarrow 2A,\ {}^3A_2^*,\ \text{or}\ A_2 \qquad (6)$$

$$A_2^* \longrightarrow A^* + A \qquad (7)$$

Since the available evidence[6,7] indicates that the excimer itself is not subject to concentration-quenching, its fluorescence yield γ_D is given by equation (II).

$$\gamma_D = \left\{\frac{k_4[A]}{k_1 + k_2 + k_4[A]}\right\}\left\{\frac{k_5}{k_5 + k_6 + k_7}\right\}, \qquad \text{(II)}$$

and those compounds exhibiting an excimer band in concentrated solutions may be expected to exhibit a similar spectrum in the molten state provided the temperature is sufficiently low to limit the dissociation process 7; at higher temperatures excimer dissociation should restore the molecular fluorescence spectrum.

This paper describes the fluorescence spectra of some low-melting derivatives of naphthalene, both in the molten state and in solution.

EXPERIMENTAL

Commercial samples of 1- (m. p. −13°) and 2-fluoro- (m. p. 61°) and 1- (m. p. −22°) and 2-methyl-naphthalene (m. p. 35°) were purified by recrystallisation or by passage through an activated-charcoal column until their fluorescence spectra in the dissolved and the molten state became independent of excitation wavelength. No emission was detected from May and Baker's chloroform under the conditions of excitation, and this solvent was used without purification. For this qualitative examination of emission spectra no attempt was made to outgas the solutions, and sealing the pure compounds *in vacuo* had little effect on the appearance of the spectra exhibited by the liquids.

Emission spectra were obtained from photoelectric recordings made on an Aminco-Keirs spectrophotophosphorimeter with the phosphoroscope cylinder removed; the slit system was that recommended for highest resolution. The independence of the recording on excitation wavelength in the range 270—290 mμ was established in each case, and the recording was corrected for the wavelength-dependent transmission of the grating monochromator and response of the 1P21 photomultiplier tube. In order to vary the temperature, sample tubes were placed in the quartz Dewar vessel supplied with the instrument, which contained distilled water or spectroscopic-grade ethanol at the appropriate temperature.

Results.—In order to identify the components of the spectrum emitted by the molten compounds, the position of molecular and excimer fluorescence bands are established by recording the spectrum of the corresponding derivative in solution, either as a function of concentration at the same temperature or as a function of temperature at constant concentration. According to equations (I) and (II) the ratio of yields γ_D/γ_M should increase with concentration or with decreasing temperature[10] which reduces the extent of excimer dissociation (process 7).

Wavelengths, λ_M, of short-wave peak in molecular spectrum and λ_D of excimer band maximum for naphthalene derivatives studied.

Substituent	System	λ_M (mμ)	λ_D (mμ)	$\nu_M - \nu_D$ (cm.$^{-1}$) (±500)	Substituent	System	λ_M (mμ)	λ_D (mμ)	$\nu_M - \nu_D$ (cm.$^{-1}$) (±500)
1-Fluoro	Solution	325	400	5770	1-Methyl	Solution	340	410	5120
	Liquid	325	405	6070		Liquid	340	407	4840
2-Fluoro	Solution	327	402	5700	2-Methyl	Solution	335	412	5570
	Liquid	327	405	5880		Liquid	328	415	6390

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[8] Stevens and McCartin, *Mol. Phys.*, 1960, **3**, 425.

[9] Stevens and Ban, unpublished work.

[10] Doller and Forster, *Z. phys. Chem.*, 1962, **31**, 274.

Figs. 1—4 show the fluorescence spectra, drawn as the wavelength-dependence of relative quanta per unit wavelength interval I_λ, for the compounds examined under the conditions stated; the I_λ scale is not necessarily the same for different spectra. The positions of λ_M, the short-wave peak of the molecular spectrum, and of λ_D, the excimer band maximum, estimated to within 2 and 5 mμ, respectively, are tabulated.

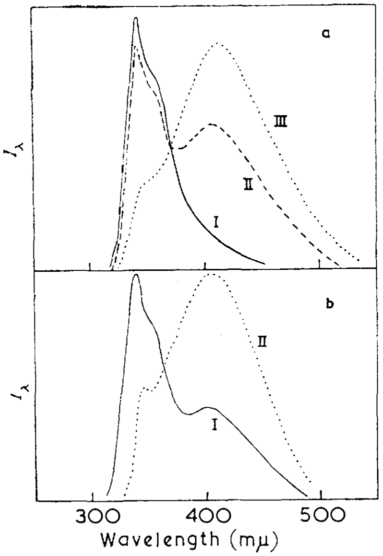

FIG. 3. Fluorescence spectra of 1-methylnaphthalene.

(a) In $CHCl_3$ at 0°: molarity = (I) 10^{-3}, (II) 0·84, (III) 4·2.

(b) Molten compound; (I) at 85°, (II) at 22°.

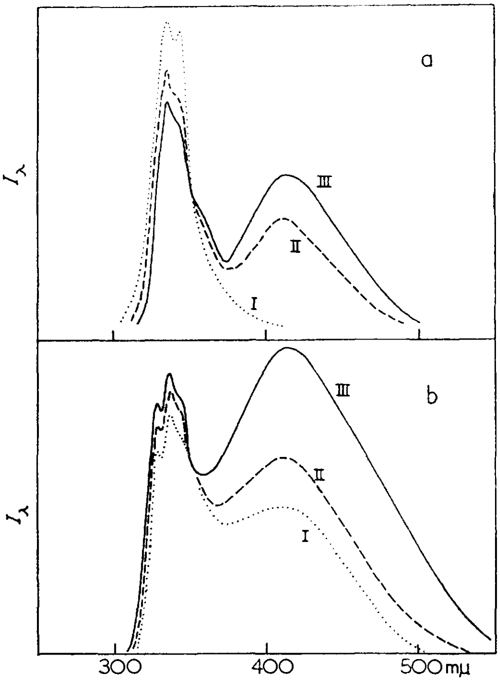

FIG. 4. Fluorescence spectra of 2-methylnaphthalene.

(a) In $CHCl_3$ at −55°: molarity = (I) 6×10^{-3}, (II) 0·25, (III) 0·49.

(b) Molten compound (outgassed): (I) at 73°, (II) at 52°, (III) at 33°.

DISCUSSION

An examination of the spectra presented in the Figures shows that: (*a*) solutions of the compounds examined emit the characteristic structureless excimer band under the appropriate conditions: (*b*) these compounds are also fluorescent in the molten state at the temperatures stated; (*c*) the excimer band is the major spectral component of fluorescence emitted by the pure liquids at temperatures near the melting point, as might be expected at these concentrations; (*d*) the ratio of intensities of the molecular to the excimer fluorescence bands increases as the temperature of the molten compound is raised; this must be attributed to a decrease in thermal stability of the excimer at higher temperatures.

In addition, the decrease in intensity of the molecular spectrum, noted at still higher temperatures ($\gtrsim$90°), must be due to a thermal deactivation of the electronically excited molecule previously reported.[11]

These observations, which are similar to those recorded for benzene and toluene,[12] provide further exceptions to the generalisation that aromatic compounds are non-fluorescent in the molten state, and indicate that the absence of fluorescence from such

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[11] Forster, *Pure Appl. Chem.*, 1962, **4**, 121.

[12] Ivanova, Mokeeva, and Sveshnikov, *Optics and Spectroscopy*, 1962, **12**, 325.

systems is rather a consequence of the high temperatures required to produce them than of the high concentration of molecules present.

Two further points of interest may be noted. If the separation of molecular and excimer emission peaks, $\Delta\nu = \nu_M - \nu_D$, is determined both by the excimer dissociation (or formation) enthalpy E_D and the repulsive potential E_R of two unexcited molecules[8] in the sandwich-like excimer configuration, then

$$h\Delta\nu = E_D + E_R.$$

Since solutions of naphthalene[10] and its derivatives studied here exhibit a well-defined excimer band only at temperatures well below that required for the same behaviour of dissolved pyrene and benzanthracene derivatives,[7] E_D must be lower for the naphthalenes than for the larger molecules. However, values of $\Delta\nu$ given in the Table are of the same magnitude as those reported for other compounds,[7] and in consequence E_R for the naphthalenes should be larger than for the pyrene and benzanthracene systems.

Secondly, the observation of the excimer band at the high molecular concentrations of the molten state confirms that this is much less susceptible to self-quenching than is the molecular fluorescence. If photoassociation is an essential step in the overall molecular self-quenching, then, by analogy, self-quenching of the excimer should require a similar interaction with an unexcited dimer of the same configuration and electronic-energy states which, by definition,[13] does not exist.[6,7] Moreover, since the energy states of the excimer and an unexcited molecule of the same species are not mutually degenerate, their interaction to form the intrinsically more stable trimer[14] may require an activation energy at least equal to that required for excimer dissociation, which would account for the absence of effects due to higher aggregates even in these molten systems.

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[13] Stevens and Hutton, *Nature*, 1960, **186**, 1045; Stevens, *ibid.*, 1961, **192**, 725.

[14] Hoijtink, personal communication.