Short Communication

A quantitative luminescence study of deuterated naphthalenes

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(Received April 12, 1973)

It is presently accepted that the rate of the radiationless transition from the first excited triplet state (T_1) to the ground state (S_0) in aromatic hydrocarbons tends to decrease upon deuteration. Some contradictory results have been reported of the effect of the position of deuterium substituents on the phosphorescence lifetimes of partially deuterated naphthalenes[1,2]. Contrary to the conclusion of Lin and Bersohn[1] that the radiationless decay to the ground state is independent of the position of the protons, Watts and Strickler[2] have found that protons in the α-position of naphthalene are 1.6 times as effective as protons in the β-position in promoting radiationless transitions. Both results have been obtained from phosphorescence decay time measurements only. Since the rate constant k_T of the $T_1 \rightarrow S_0$ transition is the sum of the rate constants of the radiative k_R and radiationless k_N pathways:

$$k_T = k_R + k_N \tag{1}$$

hence only in non-phosphorescent molecules can k_T be equal to k_N.

The exact rate of the radiationless deactivation in the case of phosphorescence can only be determined from phosphorescence quantum yield and supplemented by phosphorescence lifetime measurements, according to:

$$k_R = k_T \cdot Q_P/Q_T \tag{2}$$

where Q_T is the quantum yield of triplet formation.

In view of the importance of the positional deuterium substitution on theories of radiationless processes in aromatic molecules[3,4] and the recent reports on a deuterium effect on fluorescence quantum yields[5,6] we have measured the fluorescence and phosphorescence quantum yield as well as the phosphorescence decay time of several deuterated naphthalenes.

Experimental

The luminescence measurements were carried out with degassed solutions in EPA (diethyl ether, isopentane and ethanol, 5:5:2 by vol.) at 77 K using a recording fluoriphosphorimeter constructed in this laboratory.
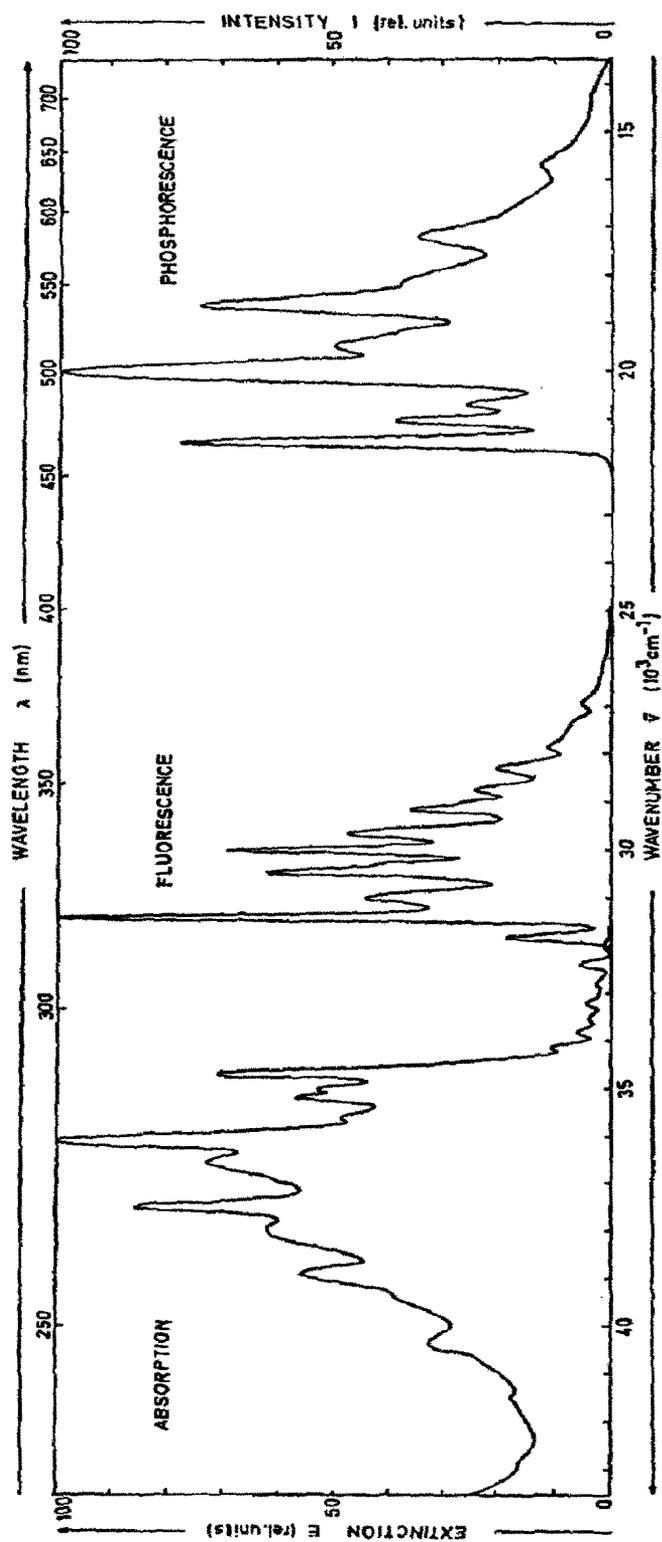
Fig. 1. Absorption and absolute fluorescence and phosphorescence spectra of naphthalene-d₈ in EPA at 77 K.

The fluorescence and phosphorescence quantum yields were evaluated from the areas under the corrected emission curves with respect to the area of fluorescence emission of quinine bisulphate in 1 N H_2SO_4 at room temperature ($\Phi_F = 0.55$)[7] and/or 9,10-diphenylanthracene in EPA at 77 K ($\Phi_F = 1.0$)[8,9]. The concentrations of the samples were adjusted to give the same absorbance at 77 K at the exciting wavelength (253.7 nm)*. Figure 1 shows the absorption, fluorescence and phosphorescence spectra of naphthalene-d_8 recorded under our experimental conditions.

The phosphorescence lifetimes were obtained by extinguishing the exciting light and following the decay of phosphorescence by means of an oscilloscope. The triplet lifetimes were investigated independently by flash spectroscopy. Naphthalene and naphthalene-d_8 (Merck) were purified by extensive zone-refining. Naphthalene-d_1, naphthalene-d_2 and naphthalene-2, 3, 4, 5, 6, 7, 8-d_7 were prepared from the Grignard reagents of the appropriate brominated naphthalenes. 1-Bromonaphthalene-d_7 and the synthesized deuterated naphthalenes were purified by column chromatography on silica gel in ligroin, the latter had melting points of 80–81°C. The isotopic purity of the naphthalenes was established by mass spectroscopy at 70 eV (see Table 1).

Results and Discussion

In the absence of a radiationless $S_1 \rightarrow S_0$ transition the radiative rate constant k_R is related to the rate constant k_T, the fluorescence and phosphorescence quantum yields Q_F and Q_P by:

$$k_R = k_T . Q_P/(1-Q_F) \tag{3}$$

The value of Q_T in eqn. (2) is replaced by $(1-Q_F)$. The non-radiative rate constant k_N is then obtained from eqn. (1). The results are summarized in Table 1.

The fluorescence quantum yields of the five naphthalenes in Table 1 are of the same value within our experimental error and are not affected by isotopic substitution indicating the absence of a radiationless $S_1 \rightarrow S_0$ transition and the absence of any significant deuterium effect on the radiationless $S_1 \rightarrow T_1$ transition and, hence, the validity of eqn. (3).

The phosphorescence quantum yields, however, increase with the number of deuterium atoms in the naphthalene molecule. In both naphthalene-h_8 and -d_8, the emission quantum yields agree fairly well with the results of Li and Lim[10], McClure et al.[11] and Parker and Hatchard[12]. Our measured phosphorescence lifetimes agree very well with those of several reported values[11,13-16].

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* We have measured phosphorescence quantum yields with errors up to over 100% between adjusting the absorbance at 77 K and room temperature! Most of the conflicting phosphorescence quantum yields reported in the literature may be due to neglect of proper absorbance adjustment at temperatures of 77 K.

TABLE 1

ISOTOPIC PURITY, LUMINESCENCE QUANTUM YIELDS, PHOSPHORESCENCE DECAY TIME AND RATE CONSTANTS OF DEUTERATED NAPHTHALENES IN DEGASSED EPA* AT 77 K

Compound	Mol**	Q_F	Q_P	τ_P (s)	k_T (s^{-1})	k_R (s^{-1})	k_N (s^{-1})
naphthalene-h_8	100	0.41	0.04	2.6	0.385	0.026	0.359
naphthalene-1-d_1	80	0.41	0.04	3.0	0.333	0.023	0.310
naphthalene-2-d_1	77	0.40	0.04	2.7	0.371	0.025	0.346
naphthalene-2, 3, 4, 5, 6, 7, 8-d_7	89	0.41	0.14	11.7	0.086	0.020	0.066
naphthalene-d_8	89	0.43	0.23	21.7	0.046	0.019	0.027

* Degassing was performed by five freeze–evacuation–thaw cycles to a pressure of less than 5×10^{-6} Torr.
** Isotopic purity. The major impurity in each case is naphthalene with one less deuterium than the primary isotope.

The 10–15% lower values for the emission yields and the phosphorescence lifetime of naphthalene-h_8 and -d_8 in EPA of Li and Lim[10] are due to the non-degassing of the solvent. Degassed samples exhibits longer lifetimes[9,17] and higher quantum yields[9].

The calculated rate constants for all the deuterated naphthalenes are similar to those reported by Watts and Strickler[2]. Since k_R remains nearly constant in all the naphthalenes investigated, only the rate of the radiationless transition k_N is influenced by deuterium substitution. This result appears not to support calculations of the radiative lifetime of the lowest triplet state of naphthalene-d_8, which is, according to Li and Lim[10], about 70% longer than that of naphthalene-h_8. Thus, we do not follow the arguments of Li and Lim[10] that there is a mass dependence of the $T_1 \rightarrow S_0$ radiative decay rate in molecules with orbitally allowed $T_1 \rightarrow S_0$ radiative transitions, an influence which never before has been observed[18-20]. Our assumption is justified through measurements on six deuterated phenanthrenes[21] which possess orbitally allowed radiative $T_1 \rightarrow S_0$ transitions. While Li and Lim[10] find a decrease of the radiative $T_1 \rightarrow S_0$ decay rate, we do not find any discernible change at all for all deuterated phenanthrenes measured[21].

We believe that the deuteration effect on phosphorescence quantum yields and the triplet state lifetime is only the result of a strong decrease of the radiationless transition probability.

The change of the non-radiative rate constant k_N depends not only on the number of the deuterium atoms but also on their position in the molecule. Following the increment calculation of Watts and Strickler[2] with the assumption that the non-radiative rate constant k_N can be expressed as

$$k_N = k_0 + N_\alpha k_\alpha + N_\beta k_\beta \tag{4}$$

for the α- and β-position in naphthalene, we obtain a $k_\alpha/k_\beta = 2.4$*, a value which is quite in line with the experimental results of Watts and Strickler[2] and the theoretical results of Henry and Siebrand[23].

We are grateful to Dr. J. Marsel from the Institute "Jozef Stefan", Ljubljana, Yugoslavia for the mass spectra of the deuterated naphthalenes.

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* In a summary on the influence of the deuterium effect on the positional deuterium substitution[22] we gave a value of $k_\alpha/k = 1.9$. This value is the mean value of two calculations for k_α/k_β between naphthalene-d_1 and -d_2 and naphthalene-h_8 and -d_1.