The Dipole Moment in the (n, π^*) Singlet-Excited State of 9, 10-Diazaphenanthrene

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It has recently been reported by several authors[1-7] that nitrogen heterocycles with the lowest singlet-excited state of an (n, π^*) type are more or less fluorescent; this is in contrast to the supposition that molecules of this kind are not fluorescent. Of these heterocycles, 9, 10-diazaphenanthrene (DAP) seems to be most suitable for a quantitative investigation of the $n \leftarrow \pi^*$ fluorescence transition, because it exhibits a relatively strong fluorescence.[1,2] This paper will report on the dipole moment of DAP in its (n, π^*) singlet-excited state; this dipole moment was evaluated from the effects of solvents on the absorption and fluorescence spectra of DAP.

The spectral data on the $n \rightarrow \pi^*$ absorption and $n \leftarrow \pi^*$ fluorescence transitions of DAP in various solvents are summarized in Table 1, where $\nu_a{}^m$ and $\nu_f{}^m$ are, respectively, the frequencies (in units of the wave number) of the absorption and the fluorescence maxima; $\delta\nu_a{}^m$ and $\delta\nu_f{}^m$ are their respective shifts, with *n*-pentane as the reference solvent; n_D is the refractive index at the sodium D line, and D is the dielectric constant. It may be seen that both absorption and fluorescence transitions are displaced to the blue with an increase in the solvent polarity, but that the shift in the fluorescence is far smaller than that in the absorption. In proton-donating solvents the absorption shift is especially large; this is attributable to the formation of a hydrogen bond between solute and solvent molecules. On the contrary, the fluorescence shows only a small blue shift. This observation leads to the conclusion that the hydrogen bond is broken in the (n, π^*) excited state.

The dipole moment in the excited state can be obtained by the application of the theory of solvent effect to the frequency shifts observed for aprotic solvents. As may be seen in Table 1, the refractive indices of the aprotic solvents employed in the present study are all of approximately the same value. Therefore, on the assumption that the dispersion term is common to all these solvents, one obtains the following equations from McRae's theory:[8]

$$\nu_a{}^m = (\text{const.})_a + \frac{2}{\boldsymbol{hc}} \frac{\mu_g(\mu_g-\mu_e)}{a^3} \frac{D-1}{D+2} \qquad (1)$$

$$\nu_f{}^m = (\text{const.})_f + \frac{2}{\boldsymbol{hc}} \frac{\mu_e(\mu_g-\mu_e)}{a^3} \frac{D-1}{D+2} \qquad (2)$$

$$\nu_a{}^m - \nu_f{}^m = (\text{const.})_{a,f} + \frac{2}{\boldsymbol{hc}} \frac{(\mu_g-\mu_e)^2}{a^3} \frac{D-1}{D+2} \qquad (3)$$

where μ_g and μ_e are the dipole moments in the ground and excited states respectively, a is the cavity radius, and $\boldsymbol{h}$ and $\boldsymbol{c}$ have the usual meanings.

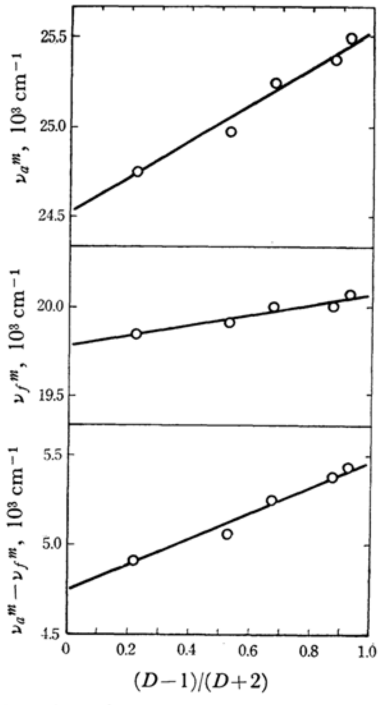

Fig. 1. Plots of $\nu_a{}^m$, $\nu_f{}^m$ and $\nu_a{}^m-\nu_f{}^m$ *vs.* $(D-1)/(D+2)$. The points from left to right represent *n*-pentane, ethyl ether, ethyl formate, acetone and acetonitrile, respectively.

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TABLE 1. SOLVENT EFFECTS ON ABSORPTION AND FLUORESCENCE SPECTRA OF 9, 10-DIAZAPHENANTHRENE

Solvent	$\nu_a{}^m$ cm^{-1}	$\nu_f{}^m$ cm^{-1}	$\delta\nu_a{}^m$ cm^{-1}	$\delta\nu_f{}^m$ cm^{-1}	n_D a)	D a)
n-Pentane	24750	19840	0	0	1.3575	1.844
Ethyl ether	24970	19910	220	70	1.3527	4.376
Ethyl formate	25250	20000	500	160	1.3599	7.16 b)
Acetone	25380	20000	630	160	1.3591	21.4
Acetonitrile	25500	20070	750	230	1.3438	37.5
Ethanol	(26200) c)	19980	(1500) c)	140	1.3614	25.00
Methanol	(26400) c)	20020	(1700) c)	180	1.3286	32.63 b)
Water	(27600) c)	20410	(2900) c)	570	1.3325 b)	78.54 b)

a) Taken from J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publishing Company, Inc., New York, N. Y. (1950); A. A. Maryott and E. R. Smith, "Table of Dielectric Constants of Pure Liquids," NBS Circular 514 (1951); "Organic Solvents."9)

b) Values at 25°C; the other values of n_D and D are at 20°C. No corrections were made for the difference between these temperatures and the experimental temperature (23±0.5°C).

c) Estimated and less reliable (see the text).

Plots of $\nu_a{}^m$, $\nu_f{}^m$, and $\nu_a{}^m-\nu_f{}^m$ against $(D-1)/(D+2)$ are found to give straight lines (Fig. 1), as is expected from the equations. From the slopes of these straight lines, the coefficients of $(D-1)/(D+2)$ in Eqs. (1)—(3) are determined to be 1010 cm^{-1}, 296 cm^{-1}, and 715 cm^{-1} respectively. Since $\boldsymbol{\mu}_e$ can reasonably be assumed to be parallel to $\boldsymbol{\mu}_g$, the ratio of the coefficients for Eqs. (2) and (1) should be equal to μ_e/μ_g. The combination of the known value of μ_g, 3.93D, with the above ratio leads to $\mu_e=1.15$D. Further, the radius, a, is determined by combining the μ_g and μ_e values with the coefficient for Eq. (3); the result is $a=4.8$ Å.

The values of μ_e and a thus obtaind are reasonable as the dipole moment in the (n, π^*) singlet-excited state and the cavity radius for DAP, and they are comparable with the corresponding values for pyridazine, $\mu_e=1.10$D and $a=3.7$ Å.7) It may be concluded that the results of the present study furnish additional evidence for the $n\leftarrow\pi^*$ fluorescence of DAP.

Experimental

9, 10-Diazaphenanthrene (Aldrich Chemical Co., U. S. A.) was recrystallized twice from a mixture of amyl acetate and petroleum ether, and purified further by chromatography with a column of fresh silica gel. All the solvents except *n*-pentane were purified by the methods described in "Organic Solvents."9) *n*-Pentane was purified chromatographically with silica gel which had been activated just before use.

Absorption spectra were obtained at 23±0.5°C by means of a Hitachi EPS-3 spectrophotometer. The fluorescence spectra were measured at the same temperature with an apparatus which had been constructed in our laboratory using a Hitachi EPU-2A prism monochromator and a Hitachi G-3 grating monochromator. Both absorption and fluorescence spectra in a hydrocarbon solvent were found to be in good agreement with those reported by Lippert *et al.*1,2)

In highly polar solvents, especially in proton-donating solvents, the $n\rightarrow\pi^*$ absorption band of DAP is greatly displaced to the blue, so that it is masked partly or almost completely by the stronger absorption band of the ^1L_b type. In such cases, the position of the $n\rightarrow\pi^*$ absorption maximum was estimated on the basis of the assumption that the shape and half-width of the absorption band remain unchanged when the solvent changes from a nonpolar to a polar substance. It should be noted that this was found to be true of the $n\leftarrow\pi^*$ fluorescence band, except when water was used as the solvent.

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