SHORT COMMUNICATIONS

EXCITED STATE DIPOLE MOMENT OF EUCHRYSINE

ASHUTOSH SHARMA and M. K. MACHWE

Department of Physics and Astrophysics, University of Delhi, Delhi 110007, India.

THE electrostatic effect of the solvent on the electronic spectra of a solute molecule provides a simple method to estimate the excited state dipole moment of a fluorescing molecule¹⁻⁵. In the present study, the effect of polar solvents on the fluorescence of euchrysine was investigated. The method adopted in this case is similar to the one used earlier¹.

The excitation and fluorescence spectra of euchrysine dissolved in various solvents (conc. $\sim 10^{-6}$ g/cc) at room temperature (20°C) are recorded using an Aminco Bowman spectrophotofluorometer. Euchrysine sample was further purified before use. Solvents used (table 1) are of analytical grade purity obtained from BDH/EM. The effect of scattering and background for each solvent was checked separately in a blank experiment and was found to be less than 0.5%. Necessary corrections were applied and the reported excitation and emisstion wavelengths are within ± 2 nm.

The following relations obtained from the theoretical considerations¹⁻⁵ are used in the interpretation of the experimental results:

$$\overline{\gamma}_a - \overline{\gamma}_f = S_1 F_1(D, n) + C_1, \qquad (1)$$

and

$$\frac{1}{2}(\overline{\gamma}_a + \overline{\gamma}_f) = S_2 F_2(D, n) + C_2, \qquad (2)$$

where $\overline{\gamma}_a$ is the absorption maxima and $\overline{\gamma}_f$ the fluorescence maxima.

$$F_1(D,n) = \left\{ \frac{D-1}{D+2} - \frac{n^2 - 1}{n^2 + 2} \right\} \frac{2n^2 + 1}{n^2 + 2},$$

$$F_2(D,n) = \frac{2n^2 + 1}{2(n^2 + 2)} \left[\frac{D-1}{D+2} - \frac{n^2 - 1}{n^2 + 2} \right] + \frac{3}{2} \frac{(n^4 - 1)}{(n^2 + 2)^2},$$

where n is the refractive index and D is the dielectric constant.

$$S_1 = \frac{2(\mu_e - \mu_g)^2}{a^3 hc}$$
 and $S_2 = \frac{-2(\mu_e^2 - \mu_g^2)}{a^3 hc}$,

where μ_e and μ_g are respectively the excited state and the ground state dipole moments of the solute molecule and a is the Onsager cavity radius.

Further from (1) and (2), the ratio of the dipole moments in the excited and the ground state is given by

$$\mu_e/\mu_g = (S_1 - S_2)/(S_1 + S_2).$$
 (3)

In the present study $\overline{\gamma}_{exc_1}$ was found to be equal to $\overline{\gamma}_a$ and hence in using (1) and (2), $\overline{\gamma}_{exc_1}$ has been used in place of $\overline{\gamma}_a$.

Table 1 summarizes the Stokes' shift data for euchrysine. The plots of $(\bar{\gamma}_a - \bar{\gamma}_f)$ against $F_1(D, n)$ and $(\bar{\gamma}_a + \bar{\gamma}_f)/2$ against $F_2(D, n)$ are shown in figures 1, 2.

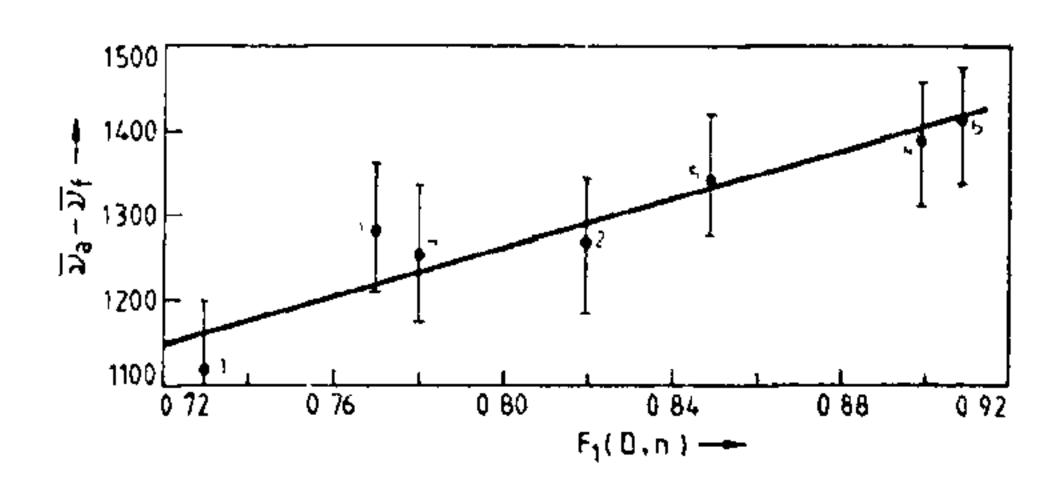


Figure 1. Stokes shift $(\overline{\gamma}_a - \overline{\gamma}_f)$ vs $F_1(D, n)$

Table 1 Stokes shift for Euchrysine in various solvents and the calculated values of $F_1(D, n)$ and $F_2(D, n)$

Solvent	λ _a nm	λ _∫ nm	ȳa cm³ ^{- 1}	γ̄ _f cm ⁻¹	$(\overline{y}_a - \overline{y}_f)$ cm^{-1}	$(\bar{\gamma}_a + \bar{\gamma}_f)/2$ cm^{-1}	$F_1(D,n)$	$F_2(\mathbf{D}, n)$
n-butanol	484	516	20661	19380	1281	20020.5	0.77	0.65
ethanol	486	518	20576	19305	1271	19940.5	0.82	0 66
iso-amyl alcohol	486	514	20576	19455	1121	20015.5	0.73	0 64
formamide	492	528	20325	18939	1386	19632.0	0.90	0.75
methanol	486	520	20576	19231	1345	19903.5	0.85	0.65
water	488	524	20492	19084	1408	19728.0	0.91	0.68
acetic anhydride	490	522	20408	19157	1251	19782.5	0.78	0.75

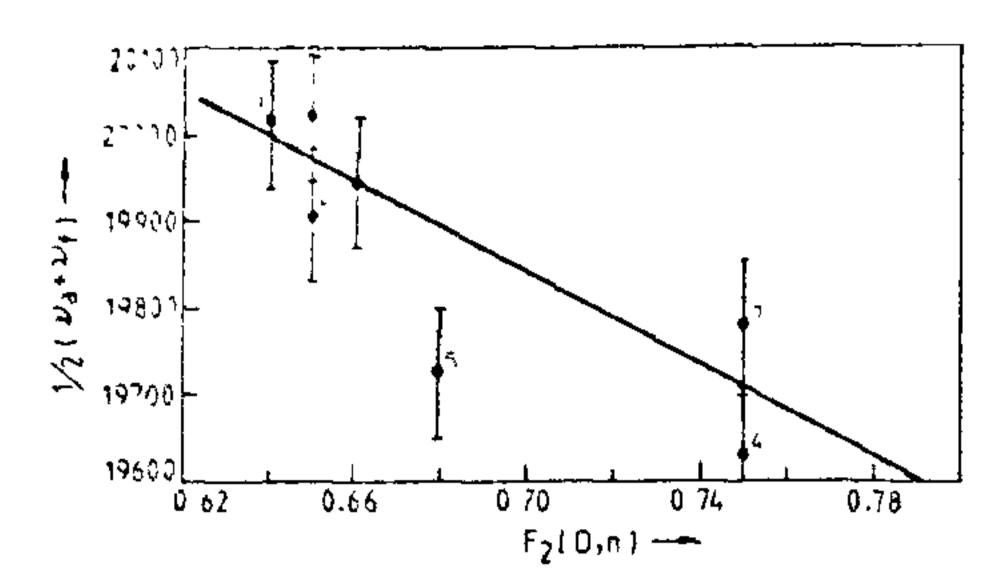


Figure 2. $\frac{1}{2}(\overline{\gamma}_a + \overline{\gamma}_f)$ is $F_2(D, n)$

These plots are linear with slopes $S_1 = 1315$ and $S_2 = -2647$. The ratio of the dipole moments in the excited state and the ground state is given by:

$$\mu_e/\mu_g = (S_1 - S_2)/(S_1 + S_2) \sim 3.0$$

i.e. $\mu_e \sim 3\mu_o$.

The excited state dipole moment of euchrysine is higher (almost three times) than the ground state dipole moment. This change in dipole moment on excitation is not very large. This could be explained from the resonance structure of euchrysine molecule (figure 3). Only structures I and II can possibly be expected to contribute to a change in dipole moment

Figure 3. Resonance structures of Euchrysine.

due to heterogeneous accumulation of charge on the amino groups. The other resonance structures viz III and IV, have a homogeneous charge distribution and would not cause much change in the dipole moment. The structure also suggests the possibility of hydrogen bonding in polar solvents via the electron pair available on the NH₂ group. This along with some other possible specific interactions could contribute to the deviation of the Stokes' shift from the linear relationship. Such effects have not been considered in the theoretical treatment of the solvent-solute interaction²⁻⁴. Also it may be noted that relation (1) is obtained on the assumption that the electric dipole moments in the ground and excited states, μ_q and μ_e are parallel. This may or may not be so in this case. Even within the framework of these limitations one finds a good agreement between the experimental results and theory.

18 April 1985; Revised 2 July 1985

- 1. Sharma, A. and Machwe, M. K., Curr. Sci., 1982, 51, 657.
- 2. Lippert, E., Z. Naturforsch, 1055, A10, 541.
- 3. Lippert, E., Z. Electrochem., 1957, 61, 962.
- Chamma, A. and Viallet, P., C.R. Acad. Sci., 1970, C270, 1901.
- 5. Bakshiev, N. G., Opt. Specktroskopia, 1964, 16, 821.

ANTIFEEDING PROPERTIES OF SWERTIA CHIRATA AGAINST JUTE SEMILOOPER (ANOMIS SABULIFERA GUEN)

R. N. MALLICK, P. C. DAS* and S. M. CHATTERJI

Jute Agricultural Research Institute,
Barrackpore 743 101, India
Chemical Research Unit, CCRAS,
Government of India, Department of Chemistry,
Calcutta University, Calcutta 700 009, India.

MANAGEMENT of crop pests with antifeedants of plant origin is still in an experimental stage in India. Some indigenous plants were reported to have effective antifeeding properties against crop pests¹⁻⁵. Anomis sabulifera was first recorded in 1906⁶ as a major pest of jute and a lot of work⁷⁻¹¹ was done on different control measures against this pest. However