

## FLUORESCENCE PROPERTIES OF BICHROMOPHORIC LASER DYES

By

É. FARKAS, M. HILBERT, I. KETSKEMÉTY and L. GÁTI  
Institute of Experimental Physics, Attila József University, Szeged

(Received 1th December, 1984)

The fluorescence characteristics of bichromophoric dyes consisting of diphenylanthracene and phenylbenzoxazole have been investigated. It was found that the efficiency of the energy transfer in this bichromophoric dye is about one hundred per cent, and the absorption oscillator of the donor includes an angle about 80 degrees with the emission oscillator of the acceptor.

Fluorescence properties of several bichromophoric laser dyes were studied by us in previous years with the aim of elucidating the energy transfer process taking place in the dyes. Parts of our results were published already [1—3]. In the hitherto investigated compounds the acceptor-moiety was identical, only the donor-moiety and the chain connecting the parts changed. The fluorescence spectra, quantum yields, and decay times of the dyes agreed with the corresponding characteristics of the compound forming the acceptor-moiety, disregarding small differences. However, considerable deviation was revealed between the polarization spectra of the acceptor and the bichromophoric dyes. On the basis of the polarization spectrum the angle between the absorption oscillator of the donor-moiety and the emission oscillator of the acceptor-moiety was found to be about 80 degrees for each compound examined. The rate of energy transfer in these molecules is greater than  $10^{12} \text{ s}^{-1}$ , as it could be proved partly by carrying out direct measurements [4] partly in an indirect manner [3].

On the basis of the results achieved to date, it has not been possible to make an unambiguous statement of character of energy transfer taking place in bichromophoric molecules [5—8]; it has, therefore, been seen suitable to extend the examinations to as wide a range of bichromophoric compounds, as possible.

In this paper account is given of the fluorescence properties of a bichromophoric dye produced in the Organic Chemistry Institute of Göttingen University under the direction of PROF. W. LÜTTKE. In the examined compound the donor-moiety is 2-phenylbenzoxazole (PBO), the acceptor-moiety diphenylanthracene (DPA) and the two moieties are joined by a group  $-\text{CH}_2-$ .

*Measurement methods, experimental results*

We recorded the absorption spectra with a spectrophotometer of the OPTON PMQ3 type, the fluorescence and polarization spectra with a fluorescence spectrometer of the PERKIN ELMER MPF44A type; the decay times were measured with an instrument constructed in our institute [9].

As solvents cyclohexane and paraffin oil produced by REANAL were used. We purified these by the usual procedure.

Figs. 1 and 2 show the absorption and emission spectra of the diphenylanthracene [DPA], and those of the bichromophoric dye consisting of 2-phenylbenzoxazole and 9,10-diphenylanthracene parts, respectively, hereinafter designated as PBO—CH<sub>2</sub>—DPA. When comparing the absorption spectra, it can be seen that in the absorption of the bichromophor, the vibration bands corresponding to the anthracene part are less sharp, and the spectrum is shifted a little towards the longer

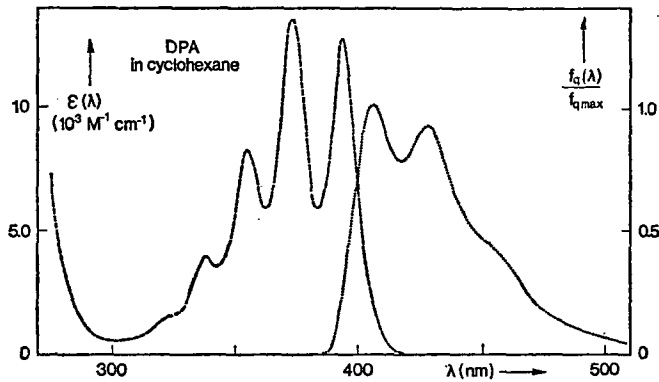


Fig. 1. Absorption and emission spectra of the DPA.

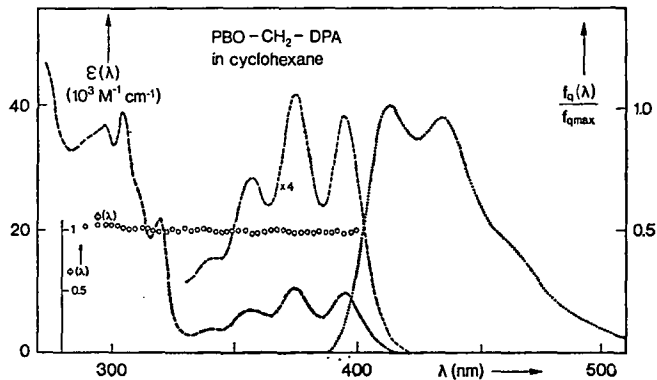


Fig. 2. Absorption and emission spectra of the PBO—CH<sub>2</sub>—DPA.  
 $\Phi(\lambda)$  is the quantum yield of fluorescence

wavelengths. The absorption band of the donor-moiety appears in the wavelength range of 280 to 330 nm; here the absorption coefficient of the DPA-moiety is very small. It can be stated, by comparison with literary data [10], that the spectrum of the donor-moiety agrees essentially with that of the 2-phenylbenzoxazole.

The fluorescence spectrum of the PBO—CH<sub>2</sub>—DPA is independent of the excitation wavelength over the excitation range of 290 to 400 nm, it is similar to the emission spectrum of DPA, but the vibration bands here are also more blurred, and a shift is observable as well, towards the longer wavelengths. It was not possible to detect the expected fluorescence of the PBO part over the wavelength range of 320 to 400 nm [10].

The quantum yield  $\Phi(\lambda)$  of the bichromophoric compound (see Fig. 2) is independent of the wavelength over the range of 290 to 400 nm, and this means that the efficiency of the energy transfer following the excitation of the donor-moiety is approximately a hundred percent.

The absolute quantum yield of the fluorescence of the PBO—CH<sub>2</sub>—DPA is equal to that of the DPA, and this latter according to [11], is practically 1.0.

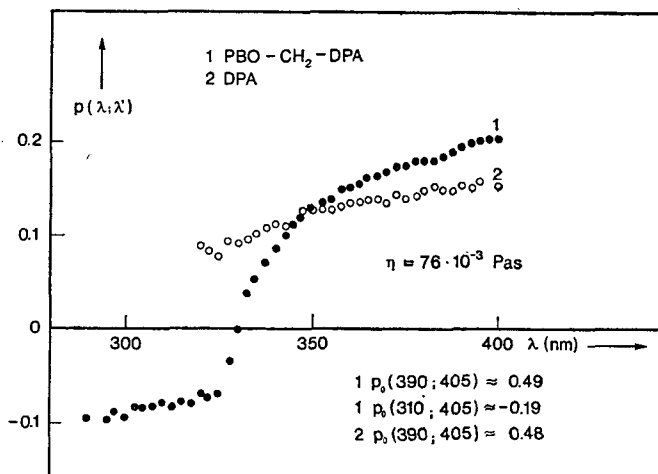


Fig. 3. Polarization spectra of the compounds in mixtures of cyclohexane — paraffin oil. The concentration of the cyclohexane is 10 percent. The temperature is 15 degrees of centigrade. The wavelength of observation is 415 nm. The concentration of the dye is  $5.10^{-6}$  M

In Fig. 3 the polarization spectra of the bichromophoric compound and of the DPA are presented. It can clearly be seen that the degree of polarization of the DPA is positive over the range of the absorption band of the donor, while that of the PBO—CH<sub>2</sub>—DPA is negative.

In order to determine the fundamental polarization value, the dependence of fluorescence polarization  $p$  on temperature  $T$  and on viscosity  $\eta$  of the solution was examined. According to Perrin—Lewshin's relation, when the decay time and the molecule volume are constant, the reciprocal  $p$  is the linear function of  $T/\eta$ , from

which the fundamental polarization  $p_0$  can be determined by extrapolation to the infinite viscosity [12].

The decay times  $\tau$  of the compounds were found identical at 22 and 35 degrees of centigrade, these values are presented in Fig. 4.

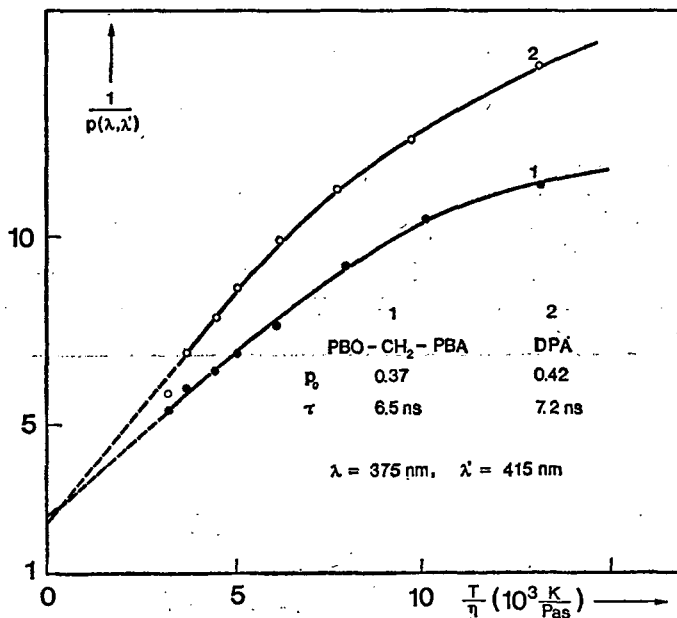


Fig. 4. The reciprocal fluorescence polarization vs  $T/\eta$ . The solvent is identical as described in Fig. 3.  $\lambda$  and  $\lambda'$  are the wavelengths of the excitation and the observation, respectively.  $p_0$  is the fundamental polarization at the given wavelengths.  $\tau$  is the decay time of the fluorescence. The concentration of the dye is  $5 \cdot 10^{-6} \text{ M}$ .

As it can be seen in Fig. 4, for the examined compounds the connection  $p^{-1} - T/\eta$  is not linear, thus the values presented there can be regarded only as approximate. On the basis of the polarization and polarized spectra it could be determined that the degree of polarization of both compounds reaches the maximum at the excitation wavelength of 390 nm and at the observation wavelength of 405 nm.

The degrees of fundamental polarization at the above wavelengths are 0.49 for the bichromophor and 0.48 for the DPA.

In the absorption band of the donor the fundamental polarization is  $-0.19$  for the PBO-CH<sub>2</sub>-DPA, from which it can be stated that the angle between the absorption oscillator of the donor-moiety and the emission oscillator of the acceptor-moiety also in this compound is approximately 80 degrees.

The spectra of the above-presented bichromophoric compounds retain the characteristics of the spectra of the component parts, which suggests a very weak interaction. The rate of energy transfer which can be calculated on the basis of the fluorescence characteristic of the donor and acceptor — supposing an interaction

of the Förster type — may be put at  $5 \cdot 10^{11} \text{ s}^{-1}$ , *i.e.* it is essentially smaller, than it was in the compounds examined earlier, and thus it may perhaps be verified by measurement subsequently. The energy transfer, in spite of the smaller rate, takes place practically without loss.

#### References

- [1] Ketskeméty, I., É. Farkas, Zs. Tóth, L. Gáti: Acta Phys. et Chem. Szeged **28**, 3 (1982).
- [2] Ketskeméty, I., É. Farkas, Zs. Tóth, L. Gáti: 4. Conference on Luminescence, Szeged 1982, p. 35.
- [3] Farkas, É., I. Ketskeméty, M. Hilbert: Summer School on Luminescence, Békéscsaba, 1982, p. 128. (in Hungarian). Marek, N., M. Bérczi, G. Vári, É. Farkas: Summer School on Luminescence, Békéscsaba, 1982, p. 144. (in Hungarian).
- [4] Kopainsky, B., W. Kaiser, F. P. Schäfer: Chem. Phys. Lett. **56**, 458 (1978).
- [5] Lüttke, W., F. P. Schäfer: Laser und Optoelektronik **15**, 127 (1983).
- [6] Liphardt, B., W. Lüttke: Liebigs Ann. Chem. **1118** (1981).
- [7] Zimmerman, H. E., T. D. Goldman, T. K. Hirzel, S. P. Schmidt: J. Org. Chem. **45**, 3933 (1980).
- [8] Schäfer, F. P., F. G. Zhang, J. Jethwa: Appl. Phys. B. **28**, 37 (1982).
- [9] Farkas, Zs., É. Farkas, I. Ketskeméty, J. Hebling, G. Szabó: (to be published in J. Lumin.)
- [10] Grudzinskiĭ, V. V., G. V. Maier, K. M. Degtyarenko and V. C. Cherkasov: Opt. i Spektrosk. (USSR) **55**, 578 (1983).  
Passerini, R.: J. Chem. Soc. **111**, 2256 (1954).
- [11] Berlman, J. B.: Fluorescence Spectra of Aromatic Molecules, Academic Press, New York, 1971.
- [12] Förster, T.: Fluoreszenz Organischer Verbindungen, Vandenhoeck et Ruprecht, Göttingen, 1951.

#### ФЛЮОРЕСЦЕНТНЫЕ ХАРАКТЕРИСТИКИ БИХРОМАТИЧЕСКИХ ЛАЗЕРНЫХ ЖИДКОСТЕЙ

*Е. Фаркаш, М. Хилберт, И. Кечкемети и Л. Гати*

Исследованы флюоресцентные характеристики бихроматических жидкостей, содержащих дифенилантрацен и фенилбензоксазол. Найдено, что к. п. д. передачи энергии в этих бихроматических жидкостях 1.0 и поглощающий осциллятор донора составляет примерно 80 градусов по эмиссионному осциллятору акцептора.