RESEARCH IN THE FIELD OF 2,4,5-TRIARYLIMIDAZOLES.

COMMUNICATION 3. SPECTRAL-LUMINESCENCE PROPERTIES
OF 1,4-BIS(4,5-DIPHENYL-1H-IMIDAZOL-2-YL)BENZENE

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In the work reported here, we continued our investigation [1, 2] of triarylimidazoles
and their derivatives, which show promise for use in formulating photosensitive materials
[3]. In order to establish the photophysical and photochemical mechanisms of reactions
taking place in these systems under the influence of light, it is necessary to interpret the
electronic absorption and emission spectra of the original molecules. Here we are reporting
on a study of the spectral-luminescence properties of 1,4-bis(4,5-diphenyl-1H-imidazol-2-yl)
benzene (I), which, according to [4], takes part in the process of photobleaching of solutions
of 1,4-bis(4,5-diphenyl-2H-imidazol-2-ylidene)2,5-cyclohexadiene [4].

\[ \text{Ph} \quad \text{N} \quad \text{NH} \quad \text{Ph} \]
\[ \text{Ph} \quad \text{NH} \quad \text{N} \quad \text{Ph} \]

EXPERIMENTAL

Compound (I), the 1,3-bis(4,5-diphenyl-1H-imidazol-2-yl)benzene, and the 2,4,5-triphenyl-
1H-imidazole were synthesized in accordance with [5-7]. The spectral-luminescence measure-
ments were performed on freshly prepared solutions of (I) at 293 and 77K. As solvents we
used purified benzene and purified 1-propanol glassed at 77K, the latter also being used for
the polarization measurements. The solution concentration was 10^{-5} M.

The absorption spectra were recorded in a Specord UV-Vis spectrophotometer. The
fluorescence spectra, the fluorescence excitation spectra, and the polarization dependences
were obtained in a Jobin Yvon JY-3 spectrofluorimeter. The phosphorescence spectra, the
phosphorescence excitation spectra, and also the polarization spectra and the dependence of
the degree of polarization P on the phosphorescence wavelength were taken in a spectrometric
unit that has been described in [8]. The degree of polarization was measured by a static
technique. As the polarizer and analyzer we used Polaroid films. In determining P, we
applied corrections for the polarizing effect of the monochromators, following [9]. The
angles between the oscillator directions were determined in accordance with [10].

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Fig. 1. Absorption spectra: a) compound (I) at 293°C in benzene (1) and in 1-propanol (2), and in 1-propanol at 77°C (3); b) absorption spectra of compounds (II) (1) and (III) (2) in 1-propanol at 293°C.

Fig. 2. Fluorescence spectrum (1) and fluorescence excitation spectrum (2) of compound (I) in 1-propanol at 293°C (a) and 77°C (b); 3) polarization spectrum (λreg 400 nm); 4) dependence of P on λemis (λexc 387 nm).

DISCUSSION OF RESULTS

The absorption spectra of solutions of (I) at 293°C in benzene and in 1-propanol are shown in Fig. 1a. In the more polar solvent, the long-wave absorption band undergoes a slight bathochromic shift (λmax is shifted from 362 nm for benzene to 367 nm for 1-propanol). At 293°C, the solutions of (I) give intense fluorescence (Fig. 2a). For proof that it is the fluorescence of (I) that is being registered, we measured fluorescence excitation spectra, which, regardless of the region of registration for the fluorescence spectrum, proved to be identical to each other and similar to the absorption spectrum of (I) (see Fig. 2a).

The low-temperature fluorescence spectrum (Fig. 2b) consists of four bands with λmax 398, 420, 445, and 473 nm, the distances between which are approximately identical (~1350 cm⁻¹). The shortest-wave band with λmax 398 nm in the fluorescence spectrum should be assigned to the purely electronic transition 0-0, the other bands to the vibronic transitions 0-1, 0-2, and 0-3. The fluorescence excitation spectrum of (I) at 77°C (Fig. 2b) has a spectrum, the distance between neighboring absorption bands also being equal to 1350 cm⁻¹. In the fluorescence excitation spectrum, the longest-wave band, with λmax 387 nm, corresponds to a purely electronic transition; the bands with λmax 368 and 351 nm are vibrational. From an analysis of the polarization spectrum and a comparison of the fluorescence spectrum with the fluorescence excitation spectrum, and also considering the magnitude of the frequency interval between the bands with 300 and 387 nm (~7700 cm⁻¹), we can ascribe the absorption band with λmax 300 nm to the individual electronic transition S0 → S2.

The degree of polarization P with registration in the 0-0 band of fluorescence and excitation and the 0-0 band of absorption of the transition S0 → S1 (Pf1 60°) is 38%, i.e., close