Photophysical Properties and Laser Performance of Photostable UV Laser Dyes

III. Sterically Hindered p-Quaterphenyls

H. Güsten and M. Rinke

H. O. Wirth
CIBA-GEIGY Marienberg GmbH, P.O. Box 1253, D-6140 Bensheim, Fed. Rep. Germany

Received 7 November 1987/Accepted 6 January 1988

Abstract. The photophysical properties such as singlet absorption and fluorescence spectra, the fluorescence quantum yield and fluorescence decay time as well as the laser performance data such as the tuning range, the conversion efficiency, and the photochemical stability of 12 sterically hindered p-quaterphenyls have been measured in ethanol and/or dioxane at room temperature. The sterically hindered p-quaterphenyls exhibit shorter laser dye emissions in the 330-380 nm range than the parent compound p-quaterphenyl. The conversion efficiencies of the sterically hindered p-quaterphenyls range between 1 and 21%. The photochemical stability of the sterically hindered p-quaterphenyls is by a factor of 10 to 20 better in dioxane than in ethanol. 2-Methyl-5-tert. butyl-p-quaterphenyl and 2, 5, 2", 5"-tetramethyl-p-quaterphenyl are among the most stable UV laser dyes known today.

PACS: 07.65, 33, 42.55, 82.50

In two earlier papers [1, 2] we have demonstrated that, on account of their photophysical and chemical properties, the alkyl substituted and ring-bridged p-quaterphenyls offer the best compromise for potential UV laser dyes. Among the p-oligophenylenes, the p-quaterphenyls meet best the requirements for a good laser dye such as:

- matching of the absorption spectrum with the emission wavelengths of the most common excimer lasers operating on XeCl (308 nm) or KrF (248 nm),
- high molar absorption coefficients at the wavelength of the excimer pump laser,
- broad spectral region of fluorescence and high fluorescence quantum yield,
- short fluorescence decay time,
- large Stokes' shift,
- little overlap of the fluorescence and triplet absorption spectral regions,
- photochemical stability,
- necessary solubility better than 10^{-3} M,
- ease of synthetic procedure.

In addition to excimer laser pumping, ring-bridged p-quaterphenyls have also been suggested for flashlamp pumping [3].

This paper reports on the photophysical properties and the characteristics of the laser performance of a sizeable number of sterically hindered p-quaterphenyls. Steric hindrance or disturbed coplanarity was introduced by methyl substitution at various positions in the phenyl rings of p-quaterphenyl.

1. Experimental Section
1.1. Photophysical Parameters
A detailed description of the techniques used to measure the photophysical properties, such as the absorption and emission spectroscopical data, the
flurorescence quantum yields and the fluorescence decay times has been given in [1, 4]. Details about the methods of fluorescence quantum yield and fluorescence decay time measurements have been published previously [5].

1.2. Laser Performance Data

The laser dye properties such as tuning range, conversion efficiency, and photochemical stability have been measured with an excimer laser (EMG 102, Lambda Physik, Göttingen) operating with XeCl or KrF in combination with a dye laser (FI 2000, Lambda Physik, Göttingen) using the oscillator stage only. Details about the technique applied to measure the laser performance data have been described recently [1, 4].

1.3. Substances

The following p-quaterphenyls have been investigated (Table 1): p-quaterphenyl (1), 3,3'-dimethyl-p-quaterphenyl (2), 2,2'-dimethyl-p-quaterphenyl (3), 3,2'-dimethyl-p-quaterphenyl (4), 3,2',3',3'-tetramethyl-p-quaterphenyl (5), 3,3',2',3'-'tetramethyl-p-quaterphenyl (6), 2,2',3',2''-tetramethyl-p-quaterphenyl (7), 2,2',2',3',3'-'tetramethyl-p-quaterphenyl (8), 2,5',2',5'-'tetramethyl-p-quaterphenyl (9), 2,6,2',6'-'tetramethyl-p-quaterphenyl (10), 2,5,2',5'-'tetramethyl-p-quaterphenyl (11), 2,2',5',5''-di tert. butyl-p-quaterphenyl (12), 2-tert. butyl-p-quaterphenyl (13), 2,3,5,6,2',3',5',6',2',3',5',6',2',3',5',6',5',6'',6',2',3',3', hexadecamethyl-p-quaterphenyl (14). Compounds 2 to 9 have been synthesized previously by Wirth et al. [6, 7]. Compounds 10-12 were generously supplied by Dr. H. Gerhardt.

2. Results and Discussion

2.1. Photophysical Properties

The photophysical data of the sterically hindered p-quaterphenyls, such as the maximum of the electronic absorption $\lambda_{\text{max}}^e$, the molar decadic absorption coefficient $\epsilon$ at the maximum of absorption as well as at the wavelength of excimer laser emission (XeCl: 308 nm, KrF: 248 nm), the maximum of the fluorescence spectrum $\lambda_{\text{max}}^f$, the fluorescence quantum yield $Q_f$, and the fluorescence decay time $\tau_f$ are summarized in Table 1. To illustrate the relative position of the singlet absorption, fluorescence emission, and triplet absorption spectra of the sterically hindered p-quaterphenyls, these three spectra of 2,2''-dimethyl-p-quaterphenyl (3) are given in Fig. 1. The singlet absorption spectra of all p-quaterphenyls investigated do not exhibit any fine structure. The degree of sterical hindrance by the methyl groups is indicated by the value of the blue shift of $\lambda_{\text{max}}^f$ compared to the p-quaterphenyl (1) parent compound. A comparison of the absorption maxima of the sterically hindered p-quaterphenyls in Table 1 indicates that the largest hypochromatic shift is obtained when the methyl substituents are introduced in the two inner phenyl rings of p-quaterphenyl (compare 3 and 4, 4 and 7 as well as 5 and 9). Two methyl groups in the inner phenyl rings as in 4 are as effective as four methyl groups in 7. While four methyl groups in various positions of p-quaterphenyl have only a minor effect on the fluorescence quantum yield (Table 1), 16 methyl groups as in 14, however, give rise to strong sterical hindrance. $Q_f$ as well as $\epsilon$ are drastically decreased to values of a tetramethyl substituted benzene. The larger the blue shift is the greater is the increase of $\epsilon$ for $\lambda_{248}$ at the expense of $\lambda_{308}$. Thus, due to the large blue shift of the maximum of the electronic absorption, sterically hindered p-quaterphenyls 7 to 10 cannot be pumped with an XeCl excimer laser anymore. The absorption spectra of the sterically hindered p-quaterphenyls have been shifted to shorter wavelengths to such an extent that the 308 nm emission of the XeCl excimer laser is no longer absorbed (compare also Fig. 1). In the same way, as the maximum of the electronic absorption is blue shifted, the fluorescence maximum of the sterically hindered p-quaterphenyls is also blue shifted, but not as much as the absorption maximum. This results in a larger Stokes' shift for the sterically hindered p-quaterphenyls compared to their parent compound 1. With the exception of the parent compound 1 and compound 2, the fluorescence spectra of the sterically hindered p-quaterphenyls do not exhibit any vibrational structures in ethanol or dioxane at room temperature. In general, they exhibit fluorescence spectra at room temperature, as depicted in Fig. 1 for 3. While the fluorescence decay times are well below one