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Dipole moments of phenalenone dyes determined in liquid and polymer polar media

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ABSTRACT

Dipole moments of the three phenalenone dyes (6-amino-1-phenalenone, 2-chloro-6-(3-methylamino)-1-phenalenone, 2-chloro-6-(3-hydroxypropylamino)-1-phenalenone) have been determined experimentally by means of a solvatochromic method and Bakshiev's, Kawski-Chamma-Viallet's theoretical approach with a use of liquid solvents and polyurethane polymer matrices of different polarity. The excited states of phenalenone dye molecules are found to be more polar than the ground ones. The values of dipole moments vary in a dependence on the substituents in the phenalenone dye molecules. The comparative analysis shows a good correlation between the calculated dye parameters, obtained with a use of liquid and polymer media.

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1. Introduction

Optical phenomena, observed in organic dyes, such as fluorescence and selective absorption of light attract attention of the researchers in different fields of science and technology. Requirements for their applications determine a use of different solvents, in particular, liquids [1,2], polymers [3], liquid crystals [4] and sol-gel glasses [5]. Knowledge of dipole moments for the electron-excited molecules of the dyes is often important for the development of nonlinear optical materials, interpretations of excited state types, and also for the investigations of any photochemical transformations.

Dipole moments of the molecules in the ground (μ_g) and excited (μ_e) states are estimated from the solvatochromic shifts of absorption and luminescence spectra as a function of the solvent dielectric permeability (ϵ) and refractive index (n). Different liquid solvents with a broad range of the ϵ and n values are usually applied for these investigations [6,7].

Along with the liquid media, synthetic polymers are broadly used as matrices for the solid-state laser organic dye-based elements; this is caused by a set of their advantages over the liquid solutions. Among a wide variety of polymer matrices, used in dye lasers and optoelectronic devices [8,9] polyurethane compositions are applied increasingly [10–16]. The polyurethane polymers possess good chemical affinity for organic dyes; their diversity on the chemical content and structure allows to optimize their functional physical properties in the different equipments with their using.

Photochemical processes in the dyes are well known to be dependent on the medium properties, where they are dissolved. These properties include dielectric permeability and refraction index values [6]. The most important factor in this relation is medium polarity, which is able to affect the absorption or emission band peak positions of a dye molecule due to solvation mechanism [7,16]. The data on dipole moments of dyes in the ground and excited states is a crucial parameter, since it provides knowledge about changes in electronic charge distribution under the molecule excitation.

This work is aimed at the determination and comparison of dipole moments, investigations, prediction and improvement of photophysical properties for phenalenone dyes [17–20] in the polyurethane matrices, depending on the polarity characteristics of liquid solvents and polyurethane polymer materials. The object of our studies is also polarity effects on the absorption and fluorescence of the mentioned dyes, since long-term and efficient generation properties of organic dye-based laser elements are substantially determined by their initial luminescence spectral parameters [20] and physico-chemical characteristics of the polymer matrices [15,16].

2. Experimental

The properties of three dyes (99%, SYNTHON Chemicals GmbH) have been studied. Their structural formulae are presented in Fig. 1. All these compounds are amino-derived from the 1-phenalenone (perynaphthenone) molecule. To obtain a bathochromic shift towards the region of 532 nm coherent pumping and to broaden the spectral range, the initial 1-phenalenone molecule (its absorption maximum is 360 nm in 1,4-dioxane [19]) is doped by different substituents. The

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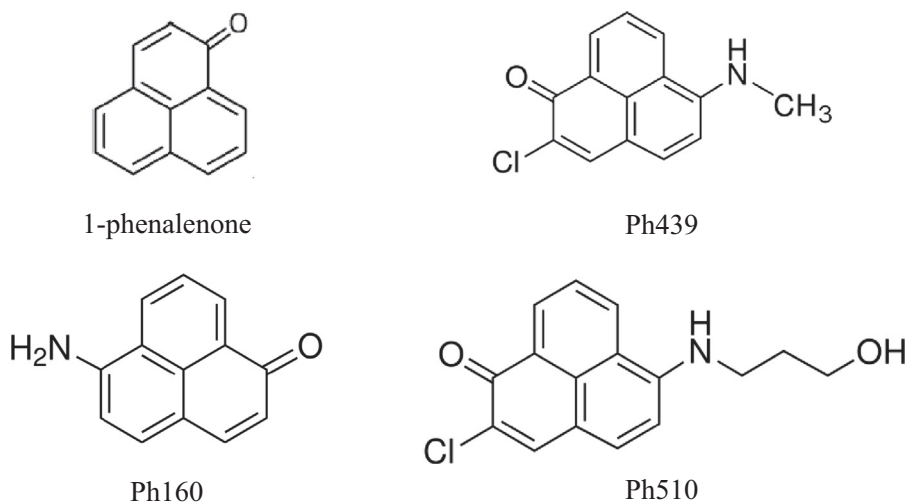


Fig. 1. Structural formulae for phenalenone dyes.

Ph160 dye (6-amino-1-phenalenone) is obtained by the insertion of a –NH₂ amino group into a position 6. The Ph439 compound (2-chloro-6-(3-methylamino)-1-phenalenone) is produced by a chlorine substituent of the 1-phenalenone molecule at a position 2 and a 3-methylamino one at a position 6. The similar way is applied for the Ph510 dye (2-chloro-6-(3-hydroxypropylamino)-1-phenalenone) synthesis.

Solvatochromic shifts of absorption and fluorescence spectra for the selected dyes have been analyzed in a dependence of different solvents, such as, butyl acetate, ethyl acetate, dichloromethane, ethanol, acetonitrile. Low-polar liquids, in particular, hexane or cyclohexane cannot be used due to the absence of phenalenone solubility in these media.

Correspondingly, along with the liquid solutions, the samples under study were both phenalenone dye doped and as-prepared pure four polyurethane (PU) matrices, produced by the polycondensation reaction for their hardening and characterized by different types of oligoether and diisocyanate components, such as:

PU-1 is based on aliphatic diisocyanate - hexamethylene diisocyanate (HMDI), oligoester diol - oligodiethylene glycol adipate (ODA) of molecular mass (MM) 800 and trimethylolpropane (TMP);

PU-2 is based on HMDI, trifunctional oligoether triol - oligooxypropylene glycol of MM 500 (OPG-500) and TMP;

PU-3 is based on HMDI, bifunctional oligoether diol - oligooxypropylene glycol of MM 1000 (OPG-1000) and TMP;

PU-4 is based on aromatic diisocyanate of 2,4-, 2,6-toluene diisocyanate (TDI) mixture, OPG-1000 and TMP.

The mentioned dyes have been also investigated in a well-studied polymer matrix, such as polyurethane acrylate (PUA), hardened by a

radical photopolymerization method of oligourethane acrylate, produced in its turn from oligooxypropylene glycol and toluene diisocyanate. The reaction of radical polymerization is carried out under a use of a photoinitiator – benzoin isobutyl ether, C₆H₅–CH [OCH₂CH(CH₃)₂–CO–C₆H₅ [21,22].

Polyurethanes, as-prepared and dye-doped at 2·10^{−4} mol/l were synthesized from the prepolymers, based on HMDI and different oligoesters, ODA, OPG-500 and OPG-1000, and also on a base of TDI and OPG-1000, taken in twofold molar exceed of diisocyanate over oligoglycol, and hardened by TMP. Dye-doped PU matrices were obtained by insertion of dye solutions in purified and dehydrated methylene chloride into the reaction mixture at the polymer formation stage. Thorough stirring was followed by vacuumizing of the reaction mixture, in order to remove air bubbles and solvent. The samples were hardened between glass or quartz substrates at the temperature 60 °C during 10–16 h.

To investigate luminescence spectral properties, the triplexes were constructed, where quartz glass was used as substrates. The thickness of the dye-activated polymer film was ~400 μm for these experiments. The optical density value, *D*₀, was about unit at a maximum of the basic transition (*D*₀ = 1.00 ± 0.05).

Absorption spectra of the dye-containing samples were recorded on a VSU-2P spectrophotometer (spectral slit width was 0.4 nm; light source was an incandescent lamp TGL-10619, 30 W) and fluorescence was measured on a Hitachi MPF-4 spectrofluorometer (spectral slit width was 1 nm; light source was a xenon lamp DL150-Xe, 150 W) at room temperature. The samples contained low concentrations of dyes ~2 × 10^{−4} mol/l, in order to decrease effects of dye self-absorption and aggregation. The spectral data were fitted by the OriginLab OriginPro 8.6 package and the MathCAD 14 was used for the calculations of dipole moments.

Dielectric permeability data was obtained by means of plain condenser capacity estimation, when studied polymer materials were applied as dielectric ones. Refractive index values were measured on an Abbe refractometer. Dielectric permeability and refractive index values for the liquid solvents were taken from the technical handbooks.

3. Results and discussion

3.1. Theoretical

The knowledge of spectroscopic parameters and dipole moments for the dye molecules is of significant interest, since it provides information about electronic and geometrical structure; it is important for the

Table 1
Photophysical parameters of the liquid solvents and polymer matrices.

Liquid solvent	Refractive index, <i>n</i>	Dielectric permeability, ϵ	Polarity (Eq. (1)), $F_1(\epsilon, n)$	Polarity (Eq. (2)), $F_2(\epsilon, n)$
Butyl acetate	1.3951	5.01	0.4118	0.4744
Ethyl acetate	1.3726	6.10	0.4934	0.5002
Dichloromethane	1.4240	8.93	0.5950	0.5852
Ethanol	1.3611	24.30	0.8117	0.6516
Acetonitrile	1.3442	37.40	0.8628	0.6659
Polymer				
PU-1	1.4898	8.8	0.5584	0.6100
PU-2	1.4900	11.2	0.6234	0.6426
PU-3	1.4708	8.2	0.5456	0.5912
PU-4	1.5002	6.6	0.4620	0.5685
PUA	1.4870	4.1	0.2840	0.4710

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