# Phenalenone derivatives as active media for dye lasers

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Spectral-luminescence and lasing properties of hydroxy- and amino-substituted phenalenones radiating in the yellow and red spectral regions are investigated under XeCl-laser excitation ($\lambda$ = 308 nm, $\tau$ = 15 ns, $W \sim 20 - 25$ MW/cm$^2$). It is shown that hydroxy-substituted molecules lase in both neutral and anion forms. Inclusion of electron donor ($NH_2$) and electron acceptor ($CF_3$) chromophores in opposite parts of the phenalenone molecule (Ph512) results in the increase of the laser efficiency (up to 27%) and photostability.

Xanthene dyes are mostly used to obtain coherent radiation in the yellow-red spectral region. It is interesting to extend the list of dyes lasing in this spectral region, in particular, to find more photostable compounds.

In this paper, we consider lasing properties of some substituted phenalenone molecules under XeCl-laser excitation. The structure formulas of molecules are given in Fig. 1.

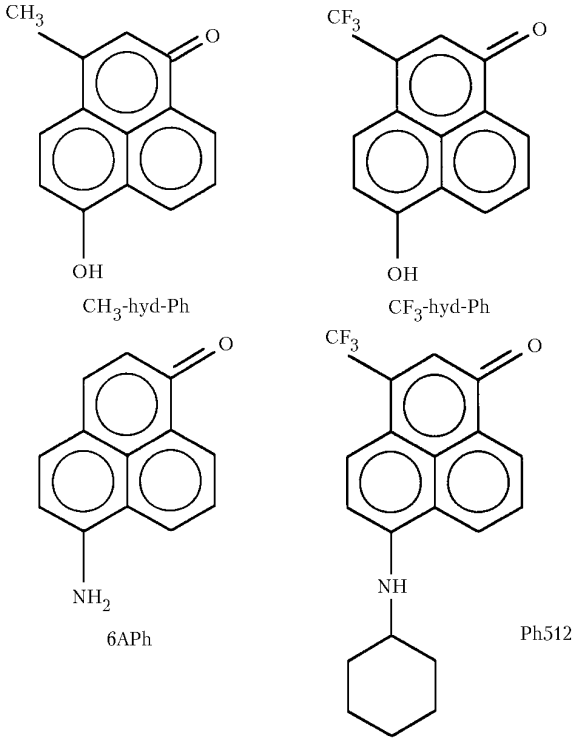


**Fig. 1.** Structure formulas of studied compounds.

## Experiment

To study spectral properties of the molecules of interest, we used a Specord M40 spectrophotometer and a Hitachi 850 spectrofluorimeter. Lasing properties and photostability were studied under excitation by XeCl laser with the following characteristics: $\lambda$ = 308 nm, $\tau$ = 15 ns, $E_p$ = 25–30 mJ. The laser radiation was focused using a cylindrical lens onto a side of a rectangular cell, and lasing was formed in the cross direction. One fully reflecting mirror and a cell side formed a cavity. Ethanol was used as a solvent. In some cases acid or alkali was added to obtain protolytic forms of studied molecules. The lasing efficiency was studied at the concentration varying from $(0.5–5)\cdot10^{-3}$ M.

The quantum yield of fluorescence was studied by the standard method.[1] As a reference, we used rhodamine 6G with the quantum yield of fluorescence $\varphi$ = 0.94 and coumarine 153 with $\varphi$ = 0.38 (Ref. 2).

The photostability of compounds was estimated by the equation $\gamma = N_{ph}/N^*$, where $\gamma$ is the quantum yield of phototransformations, which characterizes the molecular photostability of the compounds; $N_{ph}$ is the number of molecules underwent phototransformations per unit volume; $N^*$ is the number of light quanta absorbed by the unit volume of solution. The value of $N_{ph}$ was determined from variation of the intensity of the longwave absorption band of the studied compound, and $N^*$ was determined through re-calculation of the thermal energy into the number of quanta. Besides this characteristic, the service life of the active medium $P_{0.5}$ was determined as the amount of energy pumped into the unit volume of solution for the time, during which the lasing efficiency was halved. The service life of the active medium depends not only on the molecular photostability, but also on the intensity of absorption by decay products in the pump and lasing regions.[3]

## Results and discussion

Hydroxy-substituted phenalenone molecules ($CH_3$-hyd-Ph and $CF_3$-hyd-Ph) are characterized by the existence of two protolytic forms: non-dissociated form (NF) and anion (A) produced through proton separation from hydroxy-group, in neutral ethanol or water solutions. The degree of dissociation increases at

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the transition from methyl-substituted molecule to its fluorinated analog, as well as at the increase of the water fraction in solution. The fact that the fluorinated analog has more acid properties is confirmed by the obtained values of pKa acidity. For $CH_3$-hyd-Ph pKa = 7.8, and for $CF_3$-hyd-Ph pKa = 6.7.

Slight alkalization of the solution ($10^{-3}$ M NaOH) leads to complete dissociation of molecules.

As some acid is added to the solution, the ion-neutral equilibrium shifts toward NF production, and in $CH_3$-hyd-Ph all molecules transit to NF at much lower acid concentration (~ $10^{-5}$ M HCl) than in $CF_3$-hyd-Ph ($10^{-2}$ M HCl). The further increase of the acid concentration in the solution is accompanied by production of cation (C), whose absorption band lies between NF and A absorption (Fig. 2). For fluorinated phenalenone the pattern is quite similar, but absorption spectra are shifted to the red region by 5–10 nm.

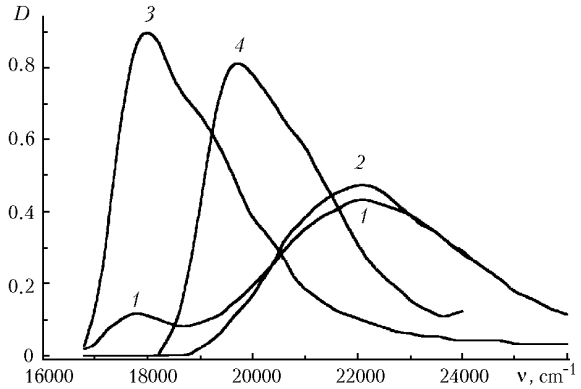


**Fig. 2**. Absorption spectra of protolytic forms of $CH_3$-hyd-Ph: in ethanol (*1*), in ethanol + $10^{-5}$ M HCl (NF) (*2*), in ethanol + $10^{-3}$ M NaOH (A) (*3*), in ethanol + volume 30% of HCl (C) (*4*).

**Table 1. Spectral properties of protolytic forms of substituted phenalenone molecules**

| Protolytic forms | $\lambda_{abs}$, nm | $\lambda_{fl}$, nm | φ | pKa |
|---|---|---|---|---|
| $CH_3$-hyd-Ph | | | | |
| Neutral | 450 | 545 | 0.66 | – |
| Anion | 550 | 590 | 0.25 | 7.8 |
| Cation | 505 | – | – | 0.4 |
| $CF_3$-hyd-Ph | | | | |
| Neutral | 454 | 550 | 0.1 | – |
| Anion | 568 | 595 | 0.42 | 6.7 |
| Cation | 520 | – | – | 0.1 |
| 6APh | | | | |
| Neutral | 540 | 597 | 0.18 | – |
| Cation | 526 | 568 | – | 0.5 |
| Dication | 403 | – | – | −1.05 |
| Ph512 | | | | |
| Neutral | 561 | 605 | 0.53 | – |
| Cation | 512 | 575 | – | 0.6 |
| Dication | 423 | 510 | – | −1.0 |

Note. $\lambda_{abs}$ is the maximum of the absorption band; $\lambda_{fl}$ is the maximum of the fluorescence band.

Spectral characteristics, quantum yield of fluorescence (φ), and emittance for NF and A are given in Table 1. We failed to determine the quantum yield of fluorescence for the cation of these compounds, because it is unstable in the excited state, gives a proton back to the medium and forms NF even at the acid content in the solution up to 80%. The emittance is almost unchanged in this case, what is indicative of the complete dissociation of the cation for the lifetime of the excited state.

Replacement of the hydroxy group with the amino group results in considerable shift of absorption and fluorescence to the red region (6APh), especially, in the presence of the $CF_3$-group (Ph512). These compounds can show only basic properties and form the protolytic forms of cation and dication (DC). From the pKa values of basicity of the amino-derivatives (see Table 1) it can be seen that the ionic forms are produced at the high acid fraction in the solution. The cation and dication absorption is shifted to the blue region of the spectrum with respect to NF absorption. Figure 3 depicts the absorption spectra of protolytic forms of 6APh.

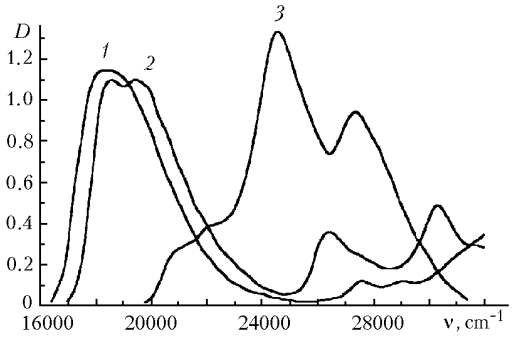


**Fig. 3.** Absorption spectra of protolytic forms of 6APh: in ethanol (NF) (*1*), in ethanol + $10^{-2}$ M HCl (C) (*2*), in ethanol + volume 80% of $H_2SO_4$ (DC) (*3*).

Absorption spectra of protolytic forms of the second amino-derivative of Ph512 are similar, but shifted to the red region by several nanometers. The lasing characteristics of the molecules are given in Table 2.

For the hydroxy-substituted molecules the lasing was obtained for two protolytic forms: NF and A. The neutral form lases in both neutral and acidified ethanol. The shift of the ion-neutral equilibrium toward NF production (acidification) leads to the increase of the lasing efficiency. This is more marked for the fluorinated analog, in which, as was mentioned above, the fraction of dissociated molecules in neutral ethanol is larger, what leads to the lower lasing efficiency (7%). The lasing efficiency becomes close for the both hydroxy-substituted molecules under the conditions of existence of only NF in the solution.

At large acid fractions, when molecules in the ground state are in the cation form, the lasing efficiency drops down (0.5%). This indicates that if in the mode of spontaneous emission the cation has time to dissociate during the lifetime of the excited state and to transit into NF, then in the mode of stimulated emission the proton transfer reaction is not complete.

**Table 2. Lasing characteristics of substituted phenalenones**

| Compound | Solvent | $\lambda_{Las}$, nm | Efficiency, % | $P_{0.5}$, J/cm$^3$ | $\gamma \cdot 10^3$ |
|---|---|---|---|---|---|
| $CH_3$-hyd-Ph $5 \cdot 10^{-3}$ M | Ethanol | 566 | 11 | 69 | – |
| | +NaOH $5 \cdot 10^{-3}$ | 599 | 11 | 60 | 3 |
| | +HCl $5 \cdot 10^{-2}$ | 577 | 13.8 | 32 | 4 |
| | +HCl 7% (volume) | 557 | 0.5 | – | – |
| $CF_3$-hyd-Ph $5 \cdot 10^{-3}$ M | Ethanol | 587 | 7 | 56 | – |
| | +NaOH $5 \cdot 10^{-3}$ | 630 | 13.8 | 86 | 2,4 |
| | +HCl 0.15 M | 584 | 14.6 | 46 | 4 |
| 6APh $2.5 \cdot 10^{-3}$ M | Ethanol | 616 | 13.5 | 80 | 6 |
| | +HCl 0.6 M | 595 | 3.5 | - | 12 |
| Ph512 $3.5 \cdot 10^{-3}$ M | Ethanol | 607 | 27 | 250* | 3 |
| | +HCl 0.6 M | No lasing | – | – | – |

Notes: $\gamma$ is the quantum yield of photodecay, $P_{0.5}$ is the active medium service life, asterisk corresponds to the 20% drop of the initial efficiency, $\lambda_{Las}$ is the lasing wavelength.

As is seen from Table 2, the protolytic forms of hydroxy-substituted molecules have close photostability. The values of the quantum yield of phototransformations ($\gamma$) range from $2 \cdot 10^{-3}$ to $4 \cdot 10^{-3}$. It should be noted that the molecules are more photostable in the anion form. The service life of these active media is also higher.

Substitution of the hydroxy group with the amino group (6APh) leads to the longwave shift of the lasing region, but the lasing efficiency and photostability remain almost unchanged. The lasing characteristics of phenalemine 512 (Ph512) improve markedly as the $CF_3$-group is introduced into the molecule and the amino group is fixed by the hexane ring. The Ph512 lasing efficiency grows up to 24–27% and the active medium service life increases considerably (see Table 2), in spite of the fact that its molecular photostability is only twice as high as compared with the other compounds. The high lasing photostability of Ph512 is explained by the lower rate of generation of photoproducts absorbing in the lasing region.

It was mentioned above that amino-substituted phenalenones are capable of forming the protolytic forms as the medium pH varies. Acidification of ethanol solutions, at which the molecules transit into the cation form, is accompanied by the drastic drop of the efficiency up to complete suppression of lasing in the both compounds.

Thus, this study has shown that the substituted phenalenone molecules can serve as active media for the yellow-red spectral region. The hydroxy-substituted molecules are capable of lasing in two protolytic forms: neutral form and anion, with the efficiency up to 14%. The amino-substituted molecules lase only in the neutral form. The most promising compound is phenalemine 512 as far as concerned both the lasing efficiency and photostability.

## Acknowledgments

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## References

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