1728 Russian Chemical Bulletin, International Edition, Vol. 63, No. 8, pp. 1728—1733, August, 2014

Molecular rotors based on styryl dyes. Viscosity dependence of rotation of molecular fragments

V. V. Volchkov,[a]* M. N. Khimich,[a] L. D. Uzhinova,[a] B. M. Uzhinov,[a]† M. Ya. Mel´nikov,[a] S. P. Gromov,[a,b]* A. I. Vedernikov,[b] S. K. Sazonov,[b] and M. V. Alfimov[b]

[a]Chemistry Department, M. V. Lomonosov Moscow State University,
Building 3, 1 Leninskie Gory, 119991 Moscow, Russian Federation.
Fax: +7 (495) 932 8846. E-mail: volchkov_vv@mail.ru
[b]Photochemistry Center, Russian Academy of Sciences,
7A-1 ul. Novatorov, 119421 Moscow, Russian Federation.
Fax: +7 (495) 936 1255. E-mail: spgromov@mail.ru

Three donor—acceptor styryl dyes R—Het$^+$—CH=CH—C_6H_4—NR´R″ClO_4^- (Het is pyridyl) were synthesized. Their spectral-luminescence behavior allows their assignment to a class of molecular rotors. The influence of the viscosity, polarity, and temperature of the medium on their absorption and fluorescence properties was studied. A pronounced enhancement of dye fluorescence accompanied by a short-wavelength shift of the fluorescence maximum is observed with an increase in the viscosity of the medium and temperature decrease. The measurements of the fluorescence spectra of the dyes in the poly(methyl methacrylate) films at 293 and 77 K confirmed the effect of the medium viscosity on the rotation ability of molecular fragments upon photoexcitation. According to the quantum chemical calculations, in excited molecules of the styryl dyes in nonpolar solvents, molecular fragments rotate mainly about the central ethylene bond (HC$\overset{...}{-}$CH). In polar solvents, the rotation barriers around the ordinary bonds of the ethylene fragment decrease.

Key words: styryl dyes, fluorescence, viscosity, molecular rotors, quantum chemical calculations; MCSCF, MCQDPT, and PCM methods.

Serious interest in the preparation of fluorophores, which are molecular rotors, is due to the dependence of their fluorescence ability on the viscosity of the environment with the prospect of their use as sensors of local viscosity in chemical and biological systems. Molecular rotors are applied as sensors of local viscosity in chemical systems and living cells,[1] viscous flow of fluids,[2] dynamic processes accompanying polymerization,[3] and conformational changes in protein molecules.[4]

Diverse classes of molecular rotors are presently known.[5] A common feature of molecular rotors is the presence of electron-donor and electron-acceptor groups and the conjugation chain between them in the structure of the molecule. These properties are characteristic, in particular, of styryl dyes R^1—Het$^+$—CH=CH—Ar—$NR^2_2X^-$. Compounds of this class were successfully applied[6] as molecular rotors for the determination of local viscosity in micelles of triblockcopolymer Pluronic F 127. Styryl dyes with a long hydrocarbon *N*-substituent in the heterocyclic residue are easily soluble in the intracellular medium and serve as viscosity sensors in cells *in vivo*.[7—9]

The question about bond determination in a styryl dye molecule about which the excited fragments rotate remain unanswered. Molecular rotors based on the aniline fragment differ from the julolidine molecular rotors by a greater number of bonds about which rotation and formation of TICT states (TICT is twisted intermolecular charge transfer) with different energies are possible. The possibility of rotation about three carbon—carbon bonds of the ethylene fragment of the styryl dye (two ordinary bonds and one double bond) has previously been assumed.[10] However, it was revealed later that rotation about the double bond is impossible, and the formation of the TICT state was explained by the mutual turn of the fragments about one of the ordinary bonds.[11]

Problems of the viscosity dependence of internal rotation in molecular rotors are widely discussed in literature. Many molecular rotors are classified as TICT molecules in which the efficiency of intramolecular charge phototransfer (*i.e.*, LE (locally excited) → CT (charge transfer)) depends substantially on the environment parameters. A decrease in the intensity ratio of the long- and short-wavelength fluorescence bands (I_{CT}/I_{LE}) of 4-[(*N*,*N*-dimethylamino)benzoyl]oxydodecyl methacrylate is sym-

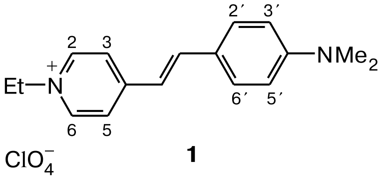
---

† Deceased.

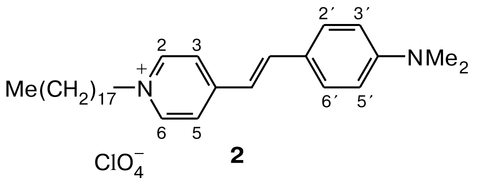
Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1728—1733, August, 2014.

bate with an increase in the size of the adjacent (to the dimethylaminobenzoyl chromophore) side polymer chain.[12] This indicates the weakening of the solvation of the TICT state in the polymer compared to the monomer, which is confirmed by the data of time-resolved fluorescence spectroscopy.[13] The fluorescence kinetics of the hemicyanine dyes in poly(methyl methacrylate) (PMMA) films indicates that the rigid environment prevents the high-amplitude motion of the fragments, blocking light emission from the relaxed state.[14] Thus, the viscosity of the environment exerts a substantial effect on the spectral-luminescence characteristics of molecular rotors.

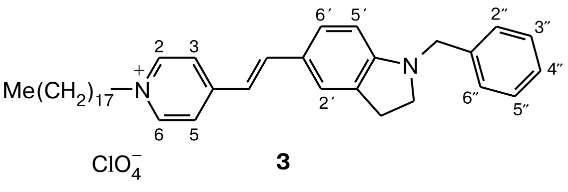
The fluorescence properties of the crown-containing styryl dyes have been studied earlier.[15,16] The purpose of the present work is to synthesize new molecular rotors based on styryl dyes **1**—**3** and to establish the influence of the viscosity, temperature, and polarity of the medium on their photorelaxation. The difference in structures of the studied compounds can be understood more deeply by the study of the dependence of the spectral-luminescence characteristics on the size of the substituent at the acceptor fragment and on the possibility of free rotation of the dialkylamino group in the benzene ring. To determine bonds about which rotation occurs, we performed the quantum chemical calculations of the dependences of the potential energy of the singlet- and triplet-excited molecule of dye **1** on torsion about one of three carbon—carbon bonds of the ethylene fragment.



1



2



3

Experimental

Melting points (uncorrected) were measured in capillaries on a Mel-Temp II instrument. ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX500 spectrometer (500.13 MHz for protons and 125.76 MHz for carbon atoms) in DMSO-d_6 and $CDCl_3$ using the solvent as an internal standard (residual protons δ_H 2.50 and 7.27, respectively; δ_C 39.43 for DMSO-d_6). Chemical shifts were measured with the 0.01 ppm, and spin-spin coupling constants were measured with the accuracy to 0.1 Hz. Heteronuclear correlation 2D ^1H—^{13}C (HSQC and HMBC) spectra were used for assignment of signals from carbon atoms. Elemental analyses were carried out at the Microanalysis Laboratory of the A. N. Nesmeyanov Institute of Organoelement Compounds (Russian Academy of Sciences, Moscow). The samples for elemental analyses were dried *in vacuo* at 80 °C.

N,*N*-Dimethyl-4-[(*E*)-2-pyridin-4-ylvinyl]aniline and 1-benzylindoline-5-carbaldehyde were obtained according to described procedures.[17,18] 1-Bromooctadecane, $NaClO_4$, 4-picoline, a 70% solution of $HClO_4$, and pyrrolidine (Aldrich) were used without additional purification.

4-{(*E*)-2-[4-(Dimethylamino)phenyl]vinyl}-1-ethylpyridinium perchlorate (1). The synthesis of dye **1** was described earlier.[19] ^{13}C NMR (DMSO-d_6, 27 °C), δ: 16.02 ($\underline{Me}CH_2$); 39.59 (NMe_2); 54.58 (CH_2N); 111.86 (C(3′), C(5′)); 117.01 ($CH{=}\underline{C}HHet$); 122.34 (C(3), C(5), C(1′)); 130.07 (C(2′), C(6′)); 141.96 ($\underline{C}H{=}CHHet$); 143.14 (C(2), C(6)); 151.82 (C(4′)); 153.59 (C(4)).

4-{(*E*)-2-[4-(Dimethylamino)phenyl]vinyl}-1-octadecylpyridinium perchlorate (2). A mixture of *N*,*N*-dimethyl-4-[(*E*)-2-pyridin-4-ylvinyl]aniline (112 mg, 0.50 mmol) and 1-bromooctadecane (167 mg, 0.50 mmol) was heated for 4 h at 140 °C (oil bath). The obtained mixture was dissolved on heating in EtOH (5 mL) and then cooled to 5 °C. The formed precipitate was filtered off, washed with EtOH (2×1 mL), and dried in air. Bromide salt of the dye was obtained as a red powder in a yield of 230 mg (82%). The bromide salt (130 mg, 0.23 mmol) was dissolved on heating in EtOH (5 mL), $NaClO_4$ (42 mg, 0.34 mmol) was added, and the obtained mixture was cooled to 5 °C. The formed precipitate was filtered off, washed with EtOH (2×1 mL) and then with Et_2O (2×2 mL), and dried in air. Dye **2** was obtained as a dark red powder in a yield of 110 mg (83%), m.p. 193—194 °C. Found (%): C, 68.99; H, 9.52; N, 4.98. $C_{33}H_{53}ClN_2O_4$. Calculated (%): C, 68.66; H, 9.26; N, 4.85. ^1H NMR ($CDCl_3$, 25 °C), δ: 0.89 (t, 3 H, $\underline{Me}CH_2$, $J = 6.9$ Hz); 1.21—1.39 (m, 30 H, $(CH_2)_{15}$); 1.96 (m, 2 H, $C\underline{H_2}CH_2N$); 3.12 (s, 6 H, NMe_2); 4.48 (t, 2 H, CH_2N, $J = 7.1$ Hz); 6.98 (d, 1 H, $CH{=}C\underline{H}Het$, $J = 15.8$ Hz); 7.08 (d, 2 H, H(3′), H(5′), $J = 8.3$ Hz); 7.58 (d, 2 H, H(2′), H(6′), $J = 8.3$ Hz); 7.62 (d, 1 H, $C\underline{H}{=}CHHet$, $J = 15.8$ Hz); 7.92 (d, 2 H, H(3), H(5), $J = 5.6$ Hz); 8.52 (d, 2 H, H(2), H(6), $J = 5.6$ Hz). ^1H NMR (DMSO-d_6, 25 °C): 0.84 (t, 3 H, $\underline{Me}CH_2$, $J = 6.9$ Hz); 1.18—1.29 (m, 30 H, $(CH_2)_{15}$); 1.87 (m, 2 H, $C\underline{H_2}CH_2N$); 3.02 (s, 6 H, NMe_2); 4.40 (t, 2 H, CH_2N, $J = 7.3$ Hz); 6.78 (d, 2 H, H(3′), H(5′), $J = 8.9$ Hz); 7.17 (d, 1 H, $CH{=}C\underline{H}Het$, $J = 16.1$ Hz); 7.59 (d, 2 H, H(2′), H(6′), $J = 8.9$ Hz); 7.92 (d, 1 H, $C\underline{H}{=}CHHet$, $J = 16.1$ Hz); 8.05 (d, 2 H, H(3), H(5), $J = 6.8$ Hz); 8.76 (d, 2 H, H(2), H(6), $J = 6.8$ Hz). ^{13}C NMR (DMSO-d_6, 25 °C), δ: 13.81 ($\underline{Me}CH_2$); 21.96 (CH_2); 25.28 (CH_2); 28.24 (CH_2); 28.57 (CH_2); 28.63 (CH_2); 28.75 (CH_2); 28.90 (8 CH_2); 30.31 ($\underline{C}H_2CH_2N$); 31.16 (CH_2); 40.33 (NMe_2); 59.08 (CH_2N); 111.84 (C(3′), C(5′)); 116.97 ($CH{=}\underline{C}HHet$); 122.28 (C(3), C(5)); 122.36 (C(1′)); 130.07 (C(2′), C(6′)); 142.09 ($\underline{C}H{=}CHHet$); 143.33 (C(2), C(6)); 151.85 (C(4′)); 153.65 (C(4)).

4-Methyl-1-octadecylpyridinium perchlorate (4). A mixture of 4-picoline (1.0 mL, 0.01 mol) and 1-bromooctadecane (3.33 g, 0.01 mol) was heated for 1.5 h at 160 °C (oil bath). The reaction mixture was dissolved on heating in EtOH (6 mL), and a 70% solution of $HClO_4$ (1.0 mL, 0.012 mol) was added. The mixture was diluted with Et_2O (10 mL) and cooled to −5 °C. The formed precipitate was filtered off, washed with Et_2O (2×10 mL), and dried in air. Salt **4** was obtained as a white powder in a yield of 3.03 g (68%), m.p. 66—68 °C. Found (%): C, 64.25; H, 10.20; N, 3.13. $C_{24}H_{44}ClNO_4$. Calculated (%): C, 64.62; H, 9.94; N, 3.14. ^1H NMR (DMSO-d_6, 22 °C), δ: 0.79 (t, 3 H, $\underline{Me}CH_2$, J = 6.9 Hz); 1.15—1.28 (m, 28 H, $(CH_2)_{14}$); 1.29 (m, 2 H, $C\underline{H}_2CH_2CH_2N$); 1.92 (m, 2 H, $C\underline{H}_2CH_2N$); 2.60 (s, 3 H, $\underline{Me}Het$); 4.84 (m, 2 H, CH_2N); 7.75 (d, 2 H, H(3), H(5), J = 6.4 Hz); 9.16 (d, 2 H, H(2), H(6), J = 6.4 Hz).

4-[(*E*)-2-(1-Benzyl-2,3-dihydro-1*H*-indol-5-yl)vinyl]-1-octadecylpyridinium perchlorate (3). A mixture of salt **4** (135 mg, 0.30 mmol), 1-benzylindoline-5-carbaldehyde (71 mg, 0.30 mmol), pyrrolidine (1 droplet), and anhydrous EtOH (10 mL) was heated for 25 h at 80 °C (oil bath). The reaction mixture was cooled to 5 °C, and the formed precipitate was filtered off, washed with EtOH (2×1 mL) and then with Et_2O (2 mL), and dried in air. Dye **3** was obtained as a red powder in a yield of 180 mg (89%), m.p. 138—139 °C. Found (%): C, 72.28; H, 8.56; N, 4.07. $C_{40}H_{57}ClN_2O_4$. Calculated (%): C, 72.21; H, 8.64; N, 4.21. ^1H NMR (DMSO-d_6, 25 °C), δ: 0.85 (t, 3 H, Me, J = 7.0 Hz); 1.19—1.30 (m, 30 H, $(CH_2)_{15}$); 1.86 (m, 2 H, $CH_2C\underline{H}_2CH_2N$); 3.03 (t, 2 H, $NCH_2C\underline{H}_2Ar$, J = 8.5 Hz); 3.51 (t, 2 H, $NC\underline{H}_2CH_2Ar$, J = 8.5 Hz); 4.39 (t, 2 H, CH_2N, J = 7.3 Hz); 4.45 (s, 2 H, $NC\underline{H}_2Ar$); 6.66 (d, 1 H, H(5´), J = 8.6 Hz); 7.13 (d, 1 H, CH=C$\underline{H}$Het, J = 16.2 Hz); 7.29 (t, 1 H, H(4″), J = 7.1 Hz); 7.31—7.40 (m, 5 H, H(6´), H(2″), H(3″), H(5″), H(6″)); 7.50 (br.s, 1 H, H(2´)); 7.88 (d, 1 H, C$\underline{H}$=CHHet, J = 16.2 Hz); 8.01 (d, 2 H, H(3), H(5), J = 6.8 Hz); 8.73 (d, 2 H, H(2), H(6), J = 6.8 Hz). ^{13}C NMR (DMSO-d_6, 25 °C), δ: 13.80 (Me); 21.95 (CH_2); 25.26 (CH_2); 26.90 ($NCH_2\underline{C}H_2Ar$); 28.22 (CH_2); 28.56 (CH_2); 28.62 (CH_2); 28.74 (CH_2); 28.89 (9 CH_2); 30.29 ($CH_2\underline{C}H_2CH_2N$); 31.15 ($CH_2$); 50.39 ($N\underline{C}H_2Ar$); 51.69 ($N\underline{C}H_2CH_2Ar$); 58.96 ($CH_2N$); 105.61 (C(5´)); 116.40 (CH=$\underline{C}$HHet); 122.07 (C(3), C(5)); 123.43 (C(2´)); 123.84 (C(1´)); 127.09 (C(4″)); 127.65 (C(2″), C(6″)); 128.40 (C(3″), C(5″)); 130.56 (C(3´)); 131.25 (C(6´)); 137.27 (C(1″)); 142.35 ($\underline{C}$H=CHHet); 143.24 (C(2), C(6)); 153.65 (C(4)); 154.43 (C(4´)).

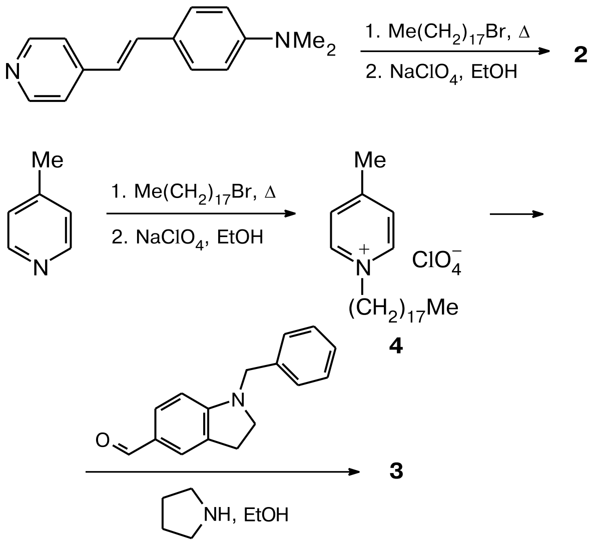
Absorption and fluorescence spectra were recorded on a UV-3100 spectrophotometer (Shimadzu) and an Elyumin-2M spectrofluorimeter. A controlled flow of liquid nitrogen vapor through the Dewar flask was used to record the fluorescence spectra at lowered temperatures. The fluorescence quantum yields (φ_f) in the range 293—77 K were calculated by comparing the areas under the corrected fluorescence spectra of the fluorophores and standards. The standards were solutions of quinine sulfate in 1 *N* H_2SO_4 (φ_f = 0.546),[20] Coumarin 522 in MeCN (φ_f = 1),[21] and Rhodamine B in ethanol (φ_f = 0.7).[22] A correction to temperature compression of the solvents was applied when calculating φ_f. Samples of the fluorophores in the PMMA films were obtained from solutions **1**—**3**/acetone/PMMA by the evaporation of acetone in the Petri dish following by film drying in air. The quartz Dewar flask, which made it possible to fix the position of the film in the cell compartment of the spectrofluorimeter, was used to record the fluorescence spectra of the films at 293 and 77 K. PMMA synthesized by radiation polymerization was used for the preparation of the films. Spectrally pure ethanol was dehydrated by distillation above CaH_2. Spectrally pure PrCN, Et_2O, and acetone were used without additional purification. Spectrally pure AcOEt was liberated from acid traces by distillation above potash.

Quantum chemical calculations were performed using the Firefly (version 8) program[23] on the MGU Chebyshev computational complex at the Research Computational Center of the M. V. Lomonosov Moscow State University. For conformational analysis in the ground and excited electron states, the geometry of the molecule was optimized by the MCSCF method (averaging over the first seven states with equal weights was used) in the 6-31 (1p, 1d) basis set at the fixed value of the corresponding torsion angle. The total energy of the molecule was determined by the MCQDPT2 method.[24] The solvation energies in ethanol and heptane were estimated by the MCSCF method in terms of PCM (Polarized Continuum Model). The values of dipole moments were determined by the xMCQDPT method.

Results and Discussion

The synthesis of dye **1** was described earlier.[19] Quaternary salt **4** and new dyes **2** and **3** were synthesized in high yields according to Scheme 1. The structures of compounds **1**—**4** were determined using the data of ^1H and ^{13}C NMR spectroscopy and spectrophotometry and confirmed by elemental analysis. All dyes were obtained as *E*-isomers (spin-spin coupling constants $^3J_{trans\text{-}CH=CH}$ = = 15.8—16.2 Hz).

Scheme 1



The absorption spectra of compounds **1**—**3** at 293 K undergo as a whole (except for dye **1** in diethyl ether) a slight short-wavelength shift on going from polar to lowly polar solvents (Table 1). Similar shifts are characteristic of the fluorescence spectra of these compounds. The Stokes shifts of the fluorescence spectra ($\Delta\lambda_{a-f}$) of the dyes are anomalously high (up to 145 nm) and depend weakly on the size of substituents in the donor and acceptor fragments. The highest values of $\Delta\lambda_{a-f}$ are observed in polar aprotic butyronitrile. The fluorescence quantum yields of compounds **1**—**3** at 293 K are low (a little higher for **2** and **3**

Table 1. Spectral-luminescence characteristics of dyes **1**—**3** in different solvents at 293 and 77 K

Dye	λ_a^{max},* Et_2O/EtOAc, PrCN/EtOH, 293 K	λ_f^{max} *		S**, Et_2O/EtOAc, PrCN/EtOH, 293 K	φ_f	
		PrCN, 77 K	Et_2O/EtOAc, PrCN/EtOH, 293 K		Et_2O/EtOAc, PrCN/EtOH, 293 K	PrCN, 77 K
1	482/462 478/481	535	592/604 621/607	100/142 143/126	0.02/0.04 0.02/0.04	0.63
2	472/466 481/484	534	589/607 623/611	117/141 142/127	0.09/0.05 0.02/0.05	0.95
3	476/482 499/500	561	594/625 644/636	118/143 145/136	0.14/0.03 0.02/0.03	0.72

* In nm.

** Here and in Table 2, S is the Stokes shift (nm).

in diethyl ether). The fixation of the position of the N atom of the amino group in the cycle (compound **3**) to prevent its rotation weakly affects the fluorescence spectra and fluorescence quantum yields compared to the unfixed amino group (compound **2**). This suggests that the possible rotation of the free dialkylamino group in molecules of the styryl dyes makes no substantial contribution to the spectral-fluorescence properties of these fluorophores.

On going from liquid butyronitrile (293 K) to the glassy one (77 K), the fluorescence spectra of the dyes experience the short-wavelength shift by 83—89 nm accompanied by a considerable increase in φ_f (see Table 1). The Stokes shifts of fluorescence of compounds **1**, **2**, and **3** in PrCN at 77 K are low: 57, 53, and 62 nm, respectively. As the temperature consecutively decreases from 293 to 77 K, the fluorescence spectra of the dyes in EtOH also demonstrate the short-wavelength shift accompanied by an increase in the intensity (Fig. 1).

The intramolecular charge transfer from the electron-donor group NR^1R^2 to the electron-acceptor residue of *N*-alkylpyridinium with the formation of the TICT state occurs upon the photoexcitation of studied compounds. This is experimentally proved by anomalously high Stokes shifts in polar solvents. The TICT state is characterized by efficient nonradiative deactivation leading to low or even zero values of φ_f. The overall process consists of the intrinsic charge transfer and mutual rotation of the donor and acceptor fragments, whose efficiency should be determined by the viscosity of the medium.

It is known[25] that an increase in the environment viscosity prevents the turn of large molecular fragments. In addition, the time of orientation relaxation of the solvent increases with the temperature decrease, which makes worse the solvation of the TICT state and decreases the probability of its formation. The character of changing the fluorescence spectra of compounds **1**—**3** in EtOH and PrCN in the range 77—293 K is completely consistent with these observations. In particular, Fig. 1 shows that the main short-wavelength shift and the increase in φ_f fall on the region of maximum viscosity increase (at the left from the glassy transition point of ethanol 159 K). In the range 150—170 K, the value of λ_f^{max} of dye **1** in EtOH shifts by 20 nm against 5 nm in PrCN (see Fig. 1, inset), which is explained by a flatter temperature dependence of the increase in the viscosity of PrCN.

The spectral-luminescence properties of the studied fluorophores depend substantially on the viscosity and temperature of the medium. The influence of the viscosity can be isolated by measuring the fluorescence spectra of the dyes in the PMMA films at 293 K and in ethyl acetate, which is close to PMMA in polarity. The fluorescence spectra of dyes **1**—**3** in PMMA exhibit the hypsochromic shift by 20—30 nm relative to the fluorescence spectra in AcOEt. The corresponding fluorescence maxima in

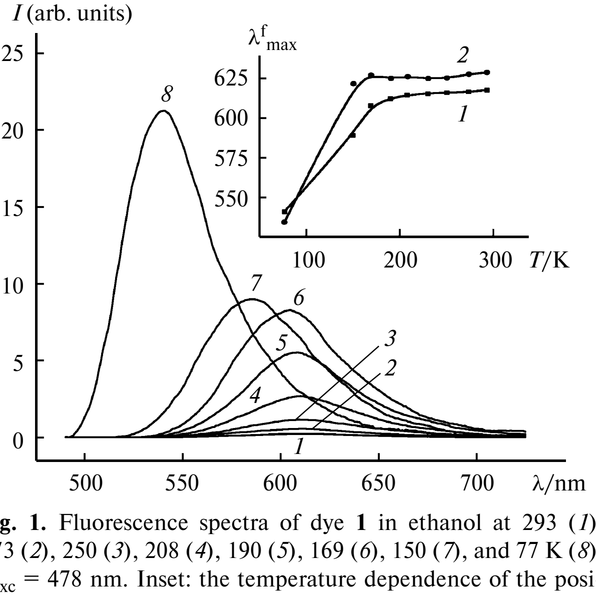


Fig. 1. Fluorescence spectra of dye **1** in ethanol at 293 (*1*), 273 (*2*), 250 (*3*), 208 (*4*), 190 (*5*), 169 (*6*), 150 (*7*), and 77 K (*8*); λ_{exc} = 478 nm. Inset: the temperature dependence of the position of the fluorescence maximum of dye **1** in (*1*) ethanol and (*2*) butyronitrile.

Table 2. Spectral-luminescence characteristics of dyes **1**—**3** in the PMMA films at 293 and 77 K

Dye	λ_a^{max} *, 293 K	λ_f^{max} * 293 K	λ_f^{max} * 77 K	*S* 293 K/77 K	φ 293 K	φ 77 K
1	473	577	560	104/87	0.18	0.28
2	476	583	566	107/90	0.62	0.72
3	494	595	580	101/86	0.71	0.75

* In nm.

PMMA and in less polar diethyl ether differ insignificantly. At the same time, a substantial increase in φ_f in the polymer is observed (Table 2). It follows from this that it is the viscosity increase that results in a decrease in the nonradiative deactivation constant, which is related to a decrease in the efficiency of TICT state formation in highly viscous media. At 77 K, the Stokes shifts of fluorescence of dyes **1**—**3** in PMMA decrease (see Table 2, Fig. 2) but do not attain the values obtained in the low-temperature glasses of PrCN. This confirms that the rotation of the molecular fragments depends on both the viscosity and polarity of the medium.

An elongation of the *N*-substituent in the acceptor moiety of the molecule results in an increase in φ_f of dyes **2** and **3** at 293 K in diethyl ether and at 293 and 77 K in PMMA compared to dye **1** (see Tables 1 and 2). Indeed, the viscous environment more efficiently blocks the turn of larger fragments, decreasing the rate constant of nonradiative deactivation. The fluorescence spectra of dyes **1**—**3** in PMMA at 77 K exhibit the short-wavelength shift (by ~15 nm) compared to the spectra at 293 K. This means that the mutual rotation of the fluorophore fragments is not completely frozen even in the solid PMMA film at 293 K.

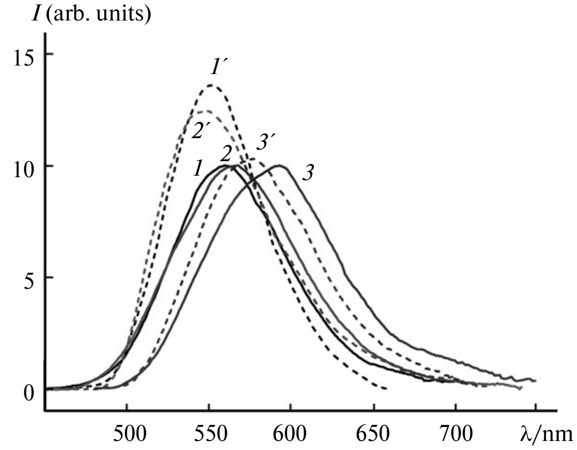


Fig. 2. Fluorescence spectra of dyes **1**—**3** in the PMMA films at 293 (*1*—*3*) and 77 K (*1′*—*3′*). All spectra were normalized to the equal fluorescence intensity at 293 K.

The quantum chemical calculations of the dependences of the potential energy in the S_0, S_1, and T_1 states on the dihedral angles at ethylene bonds *1*—*3* of the $\mathrm{Het^{+}\overset{\mathit{1}}{-}CH\overset{\mathit{2}}{-}CH\overset{\mathit{3}}{-}Ar}$ fragment were performed for the cation of dye **1**. The barrier is surmounted in the S_1 state for the mutual turn of the aromatic rings by 180° about any indicated bond (Fig. 3). Planar configurations are preferable for rotamers formed by turns about the ordinary bonds

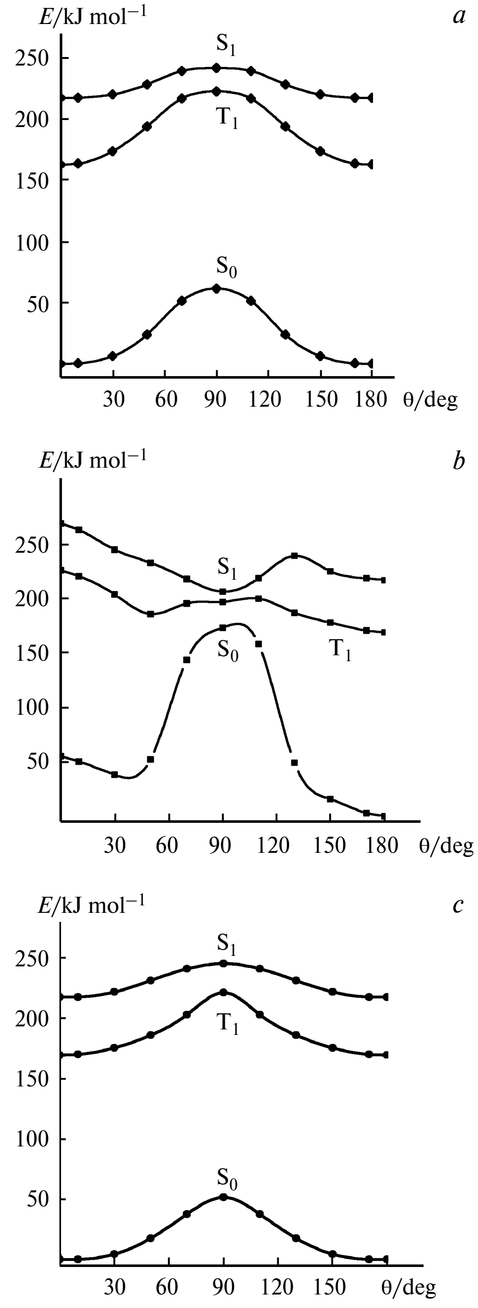


Fig. 3. Relative total energies (*E*) of the cation of dye **1** *vs* dihedral angle θ between the planes of the pyridine and ethylene fragments (*a*), fragments HetCH and CHAr (*b*), and ethylene and benzene fragments (*c*) in the S_0, S_1, and T_1 states.

Table 3. Potential barriers (E_a) and enthalpies of torsion* (ΔH_{TICT}) for the planar conformers and the dipole moments of the planar (μ) and twisted (μ_{TICT}) forms in the S_1 state of dye **1**

Bond	E_a	ΔH_{TICT}	μ	μ_{TICT}
	kJ mol^{-1}		Da	
1	24	24	5.2	11.6
2	22	−11	5.2	11.0
3	28	28	5.2	12.6

* Torsion in the fragment $\mathrm{Het}^+\overset{1}{—}\mathrm{CH}\overset{2}{=}\mathrm{CH}\overset{3}{—}\mathrm{Ar}$ about bonds *1—3*.

(see Fig. 3, *a*, *c*). Twisted forms correspond to heights of potential barriers (Table 3). The turn about bond *2* in the indicated fragment is characterized by the potential barrier at 130° and a shallow energy minimum corresponding to the twisted rotamer (see Fig. 3, *b*, Table 3). The rotation about bond *2* in molecules of the styryl dyes results in *E*—*Z*-isomerization.[26]

The absence of photoisomerization of dyes **1**—**3** can be explained by the efficient conversion $S_1 \rightarrow T_1$ in the twisted rotamer.[27] In the T_1 state, the molecule is adiabatically transformed into the planar form corresponding to the energy minimum and then it is transformed nonradiatively into the initial *E*-isomer (see Fig. 3, *b*). Taking into account solvation decreases the energy minimum of the S_1 state of dye **1** by 8 kJ mol^{-1} compared to heptane. The increase in φ_f for compounds **2** and **3** in weakly polar Et_2O compared to ethyl acetate, butyronitrile, and ethanol (see Table 1) confirms the influence of solvation on the rate constant of twisted state formation.

Thus, the quantum chemical calculations showed that in the nonpolar solvent the molecular fragments of the studied styryl dyes rotate mainly about the central ethylene bond. The rotation barriers about the ordinary bonds of the ethylene fragment decrease in polar solvents.

The substantial dependences of the spectral-luminescence characteristics of the styryl dyes $R^1—Het^+—CH=CH—C_6H_4—NR^1R^2ClO_4^-$ on the viscosity of the medium reflect rotations of the molecular fragments in them and make it possible to consider these compounds as molecular rotors. According to the quantum chemical calculations, for the barrier photorelaxation of cations of the dyes, twisting occurs about the bonds of the ethylene bridge to form weakly fluorescent TICT states. The dependences of the efficiency of the formation of the TICT states of the styryl dyes on the temperature, viscosity, and polarity of the medium were observed.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos 11-03-01026 and 13-03-12423) and the Russian Academy of Sciences.

References

1. R. Humphry-Baker, M. Graetzel, R. Steiger, *J. Am. Chem. Soc.*, 1980, **102**, 847.
2. M. A. Haidekker, W. Akers, D. Lichlyter, T. P. Brady, E. A. Theodorakis, *Sensor Lett.*, 2005, **3**, 42.
3. P. Bosch, F. Catalina, T. Corrales, C. Peinado, *Chem. Eur. J.*, 2005, **11**, 4314.
4. E. S. Voropai, M. P. Samtsov, K. N. Kaplevski, A. A. Maskevich, V. I. Stepuro, O. I. Povarova, I. M. Kuznetsova, K. K. Turoverov, A. L. Fink, V. N. Uverskii, *J. Appl. Spect.*, 2003, **70**, 868.
5. B. M. Uzhinov, V. L. Ivanov, M. Ya. Mel´nikov, *Russ. Chem. Rev.*, 2011, **80**, 1179.
6. Y. Shiraishi, T. Inoue, T. Hirai, *Langmuir*, 2010, **26**, 17505.
7. B. Wandelt, A. Mielniczak, P. Turkewitsch, G. D. Darling, B. R. Stranix, *Biosensors Bioelectronics*, 2003, **18**, 465.
8. S. K. Saha, P. Purkayastha, A. B. Das, S. Dhara, *J. Photochem. Photobiol. A: Chem.*, 2008, **199**, 179.
9. B. Wandelt, P. Cywinski, G. D. Darling, B. R. Stranix, *Biosensors Bioelectronics*, 2005, **20**, 1728.
10. B. Strehmel, H. Seifert, W. Rettig, *J. Phys. Chem. B*, 1997, **101**, 2232.
11. X. Cao, R. W. Tolbert, J. L. McHale, W. D. Edwards, *J. Phys. Chem. A*, 1998, **102**, 2739.
12. S. Tazuke, R. K. Guo, R. Hayashi, *Macromolecules*, 1989, **22**, 729.
13. S. Tazuke, R. K. Guo, T. Ikeda, *J. Phys. Chem.*, 1990, **94**, 1408.
14. J. Kim, M. Lee, J.-H. Yang, J.-H. Choy, *J. Phys. Chem. A*, 2000, **104**, 1388.
15. S. P. Gromov, O. A. Fedorova, M. V. Alfimov, S. I. Druzhinin, M. V. Rusalov, B. M. Uzhinov, *Russ. Chem. Bull.* (*Int. Ed.*), 1995, **44**, 1922 [*Izv. Akad. Nauk*, *Ser. Khim.*, 1995, 2003].
16. S. I. Druzhinin, M. V. Rusalov, B. M. Uzhinov, M. V. Alfimov, S. P. Gromov, O. A. Fedorova, *Proc. Ind. Acad. Sci.*: *Chem. Sci.*, 1995, **107**, 721.
17. L. G. Kuz´mina, A. I. Vedernikov, N. A. Lobova, S. K. Sazonov, S. S. Basok, J. A. K. Howard, S. P. Gromov, *Russ. Chem. Bull.* (*Int. Ed.*), 2009, **58**, 1192 [*Izv. Akad. Nauk*, *Ser. Khim.*, 2009, 1161].
18. A. Gazit, N. Osherov, I. Posner, P. Yaish, E. Poradosu, C. Gilon, A. Levitzki, *J. Med. Chem.*, 1991, **34**, 1896.
19. A. I. Vedernikov, L. G. Kuz´mina, S. K. Sazonov, N. A. Lobova, P. S. Loginov, A. V. Churakov, Yu. A. Strelenko, J. A. K. Howard, M. V. Alfimov, S. P. Gromov, *Russ. Chem. Bull.* (*Int. Ed.*), 2007, **56**, 1860 [*Izv. Akad. Nauk*, *Ser. Khim.*, 2007, 1797].
20. W. H. Melhuish, *J. Phys. Chem.*, 1961, **65**, 229.
21. K. Rechthaler, G. Köhler, *Chem. Phys.*, 1994, **189**, 99.
22. F. L. Arbeloa, P. R. Ojeda, I. L. Arbeloa, *J. Luminesc.*, 1989, **44**, 105.
23. A. A. Granovsky, *Firefly Quantum Chemistry Package*, Version 8.0; http://classic.chem.msu.ru/gran/firefly/index.html
24. A. A. Granovsky, *J. Chem. Phys.*, 2011, **134**, 214113.
25. M. K. Kuimova, M. Balaz, H. L. Anderson, P. R. Ogilby, *J. Am. Chem. Soc.*, 2009, **131**, 7948.
26. G. D. Titskii, T. S. Gaidash, V. N. Matvienko, A. A. Matveev, *Theor. Exp. Chem.*, 2002, **38**, 179.
27. L. S. Atabekyan, N. A. Lobova, A. I. Vedernikov, S. P. Gromov, A. K. Chibisov, *High Energy Chem.* (*Engl. Transl.*), 2012, **46**, 100 [*Khim. Vys. Energ.*, 2012, **46**, 142].

Received January 21, 2014;
in revised form June 2, 2014