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Low Temperature Spectra of the *ortho*-POPOP Molecule: Additional Arguments of Its Flattening in the Excited State

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Low temperature absorption and fluorescence spectra were measured for 1,2-bis-(5-phenyl-oxazolyl-2)-benzene (*ortho*-POPOP), a sterically hindered molecule, substantially non-planar in its ground state. Quantum-chemical calculations with the optimization of molecular geometry were made using the semiempirical AM1 method. The observed spectral changes, together with the obtained theoretical results, evidenced in favor of our previously made assumption about the considerable flattening of *ortho*-POPOP in the lowest singlet excited state. The data of spin-orbit coupling between singlet and triplet terms, which has been estimated in CNDO/S scheme, were used to calculate the efficiency of intersystem crossing in the studied molecule.

KEY WORDS: *ortho*-POPOP; absorption and fluorescence low temperature spectra; primary photophysical processes; spin-orbit coupling; excited state structural relaxation.

INTRODUCTION

Organic luminophores, which can emit fluorescence with abnormally high Stokes shift, seem to have more advantages in comparison with the traditional ones. This is because of the noticeable decrease of light losses due to reabsorption and/or with absorption of environment and also with absorption of probable photoproducts, which formed under conditions of continuous ultraviolet irradiation [1–3].

The main reason for the appearance of the abnormally high Stokes shift in luminescene is due to photophysical, or, more likely, photochemical processes, which lead to the considerable lowering of the energy of the excited state. The number of such processes known to the present time is limited, and most of them can not be used in scientific and technical applications, which demand considerable increase in light output. The main requirement to such photophysical or photochemical process, is the low level of radiationless losses, which are induced by it. The best-known intramolecular processes, which result in the emission of fluorescence with abnormally high Stokes shift, are the excited state proton transfer reaction (ESIPT) [4–10] and structural relaxation, which leads to the formation of highly polar excited states with the considerable separation of charges (TICT states) [11–15]. Unfortunately, in these cases a noticeable fraction of the initially excited molecules returns to their ground state via radiationless channels: fluorescence quantum yields of the most of ESIPT or TICT molecules rarely exceed 0.1.

During several last years we have been studying an interesting class of compounds, which demonstrate both high fluorescence efficiency (φ_j ~0.5–0.6) and abnormally high Stokes shifts values (8000–9000 cm^{-1}) - the sterically hindered aryl derivatives of oxazole and oxadia-

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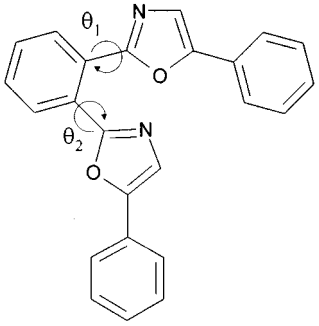

Scheme 1.

zole - analogues of 1,2-bis-(5-phenyl-oxazolyl-2)-benzene (*ortho*-POPOP) [16–20]. Two bulky hetaryl groups, which are introduced into the ortho-positions of the central phenylene nucleus, result in the formation of highly unplanar and asymmetric molecular configuration, in which angles θ_1 and θ_2 differ considerably one from another (Scheme 1).

In our previous articles we have investigated the X-ray molecular structure of the title compounds, their spectral properties and dynamics of the excited state structural relaxation process, which is the reason for the observed high fluorescence Stokes shift. Basing on the results of our experiments, we made the assumption, that the substantially non-planar molecules of *ortho*-POPOP class undergo considerable flattening in their excited state.

In the present paper we will make an attempt to find out both experimental and theoretical evidence in favor of this assumption.

EXPERIMENTAL

Synthesis, identification and purification of the investigated compound, *ortho*-analog of POPOP, were described in our previous articles [16–20].

Low temperature electronic absorption spectra in propanol-1 were measured on Shimadzu UV 3100 spectrophotometer, while the emission spectra were recorded on Jasny spectrofluorimeter [21], both equipped with low temperature accessories.

Quantum-chemical calculations by the AM1 semiempirical method [22] were made with the use of MOPAC 6.0 program. Optimization of molecular geometry in the ground and in the lowest excited singlet states was made by the 'eigenvector following' routine. Excited states energies and properties were calculated for the AM1-optimized structures by the specially developed program, which realizes the traditional CNDO/S CI routine [23] and allows to evaluate spin-orbit coupling between singlet and triplet excited states. The overlap correction factors for the resonance integrals were introduced according to the recommendations of [23]. Coulomb integrals $\gamma_{\mu\nu}$ were calculated by Mataga-Nishimoto formulae [24]. Up to 100 singly excited configurations were usually taken into account during the CI calculations (10 occupied and 10 vacant MOs were taken into consideration). The matrix elements of spin-orbit coupling operator (β_{ij}) were estimated according to [25] (single- and two-electron contributions, single-, two- and three-centered integrals were taken into account [25]). The β_{ij} values were further used for the calculation of the rate constants of intersystem crossing (k_{ISC}) by the scheme, in which the interaction of fluorescent state (S_1^*) with all the lower lying triplet states was considered to calculate the total value of $k_{ISC} = \sum_{j=1,n} k_{1j}$. The primary intersystem crossing rate constants for the above summation were estimated by the empirical Robinson and Frosch equation [26]: $k_{1j} = 0.71 \cdot 10^{12} \cdot \beta_{1j}{}^2 \cdot exp(-0.25 \cdot \Delta E_{1j}^{0.4})$, in which indices 1 and j are related correspondingly to S_1^* and any lower lying T_j^* states, ΔE_{1j} (cm^{-1}) is the energy difference between these singlet and triplet levels. The fluorescence radiative rate constants were calculated from the energy and oscillator strength values for S_0-S_1^* transitions, obtained from CNDO/S CI calculations.

RESULTS AND DISCUSSION

As it was shown in our previous articles [16–20], a substantial sterical hindrance is typical for the molecule of *ortho*-POPOP. The introduction of two oxazolic cycles into the *ortho*-positions of central phenylene ring results in formation of considerably nonplanar and asymmetric structure. The angles between the planes of the two heterocycles and the central phenylene moiety noticeably differ one from another: X-ray structural analysis reported their values of ~25° and ~70° [16,17]. Our study of vibrational (both infrared and Raman spectra) as well as electronic absorption spectra allowed us to conclude, that the conformation of the *ortho*-POPOP molecule remains nearly the same on going from crystalline state to solutions [16–20].

The results of our quantum-chemical calculations with the optimization of molecular geometry are agreed with the above assumption. The final "optimal" structure was practically independent from the initial conformation on the first step of optimization process. We used various starting points in the optimization: the planar molecule, the molecule with orthogonal heterocycles, or the X-ray

geometry. In all these cases the optimization resulted in the non-planar asymmetric structure with the angles between the planes of the heterocyclic rings and the plane of central phenylene ring equal to 33° and 59° (Fig. 1).

Thus, molecules, which belong to the class of *ortho*-POPOP derivatives, can be considered in their ground state as bichromophoric systems with two weakly interacting chromophoric fragments: diphenyloxazolyl and oxazolylphenyl. Conjugation between these fragments is decreased due to sterical reasons. In our previous articles we reported several facts in favor of this bichromophoric approach [18–20], the most important of which was the insensitivity of the absorption bands, belonging to one of the chromophoric fragments, to the introduction of substituents into another fragment.

The low temperature absorption spectra of the *ortho*-POPOP molecule in propanol-1 (its melting point is near 146K) are presented in Fig. 2. Numerous attempts of measuring the analogous spectra in the inert hydrocarbon solvent, 3-methylpentane, were failed due to the precipitation of the investigated compound at temperatures lower than 100K. The increased level of light scattering made the measurement of absorption spectra practically impossible below this temperature.

Practically very little changes in position of long-wavelength absorption band of the model compound 2,5-diphenyloxazole (PPO) were observed at low temperatures. The main temperature effect on the absorption spectrum of PPO was quite trivial: sharpening of vibrational structure and slight long-wavelength shift (up to 500 cm^{-1}). Analogous behavior could be expected for the para isomer of the title compound—1,4-bis-(5-phenyl-oxazolyl-2)-benzene (POPOP). The Stokes shift values for these two compounds were low at room temperature, and no significant changes in positions of their emission bands might be expected at decreasing of temperature.

In one of our previous articles [18] we made a series of calculations of hypothetical *ortho*-POPOP conformers, which differ one from another by the mutual orientation of their two oxazole cycles (to obtain all the molecular geometries for that calculations the oxazole cycles were rotated around the ordinary bonds, which connect them to the central phenylene in the range from 0 to 180 degrees with the step of 10°). The considerable dependence of the electronic absorption spectra of the ortho POPOP from the mutual orientation of its two oxazole cycles was found in those calculations. Three electronic transitions were situated in the range of 26000–40000 cm^{-1}. Their positions and relative intensity were strongly determined by the molecular conformation (only a few examples: S_0–S_1 transition changes its position from ~27000 cm^{-1} for the flatten molecule to the ~34000 cm^{-1} for the "fully-orthogonal" structure. Its intensity decreases more than 2–3 times on such conditions. S_0-S_3 transition, which is well resolved in the flatten symmetric structure, became forbidden at the increase of non-planarity. The S_0–S_2 transition behaves similarly to S_0–S_1 one). In [18] we have built three-dimensional surface, which displayed the existed connection between the correlation function, calculated on the base of theoretical and experimental

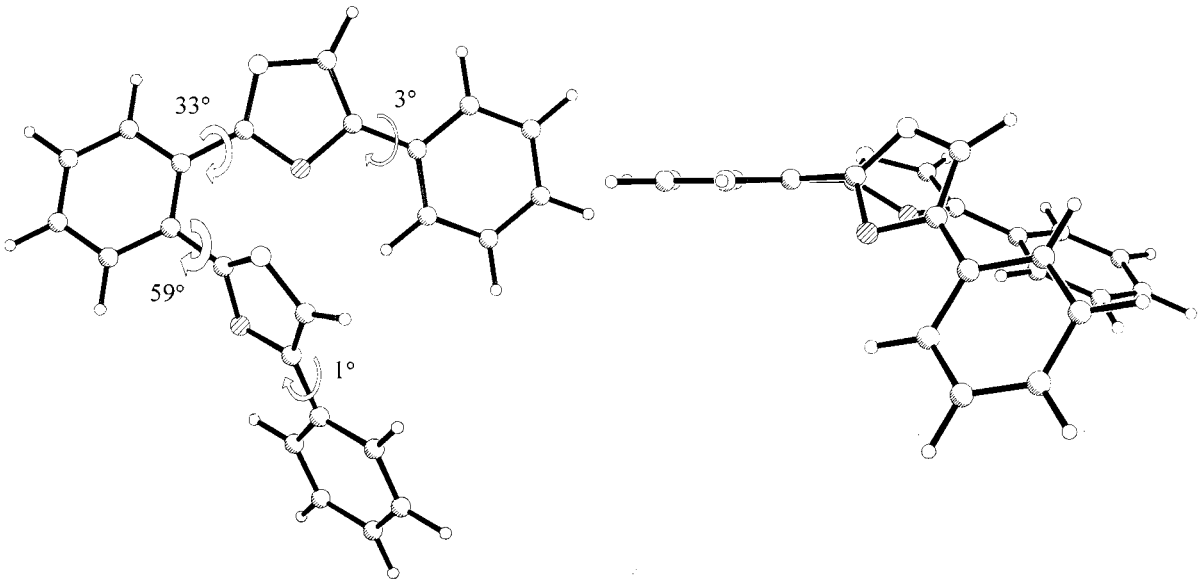

Fig. 1. Optimized ground state structure of *ortho*-POPOP molecule (in two projections). Angles between the planes of benzene- and hetero-cycles are shown near the correspondent single bonds.

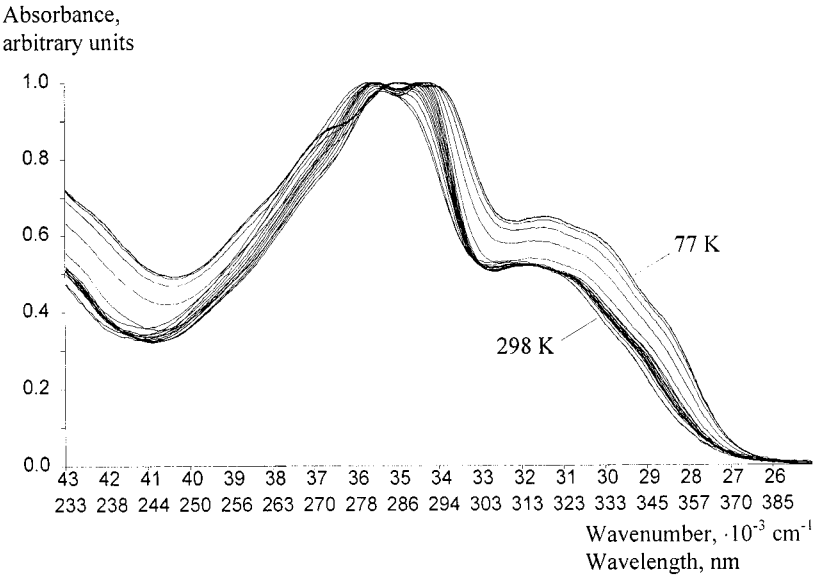

Fig. 2. Low temperature absorption spectra of *ortho*-POPOP in propanol-1 at the following temperatures: 298, 263, 228, 209, 203, 193, 183, 173, 163, 153, 143, 133, 123, 113, 103, 93, 88, and 77 K.

spectra, from the conformation of the ortho-POPOP molecule. Two points of the maximal correspondence between the theoretical and the experimental spectra, which belong to two possible optical isomers of the ortho-POPOP molecule, were found on that surface. Both of them were closely correspond to the X-ray conformation.

Based on the data presented in Fig. 2 and also taking into account the results reported in [18], we can make a conclusion, that non-planar and asymmetric conformation of *ortho*-POPOP molecule does not change considerably with the decrease of temperature down to that of liquid nitrogen. Low temperature absorption spectra of *ortho*-POPOP in solidified propanol-1 reveal a little better pronounced vibrational structure, which reflects the decrease of probability of intramolecular vibrations. However, the energies and relative intensities of two resolved long-wavelength electronic transitions, which depend considerably on the mutual orientation of the two heterocycles

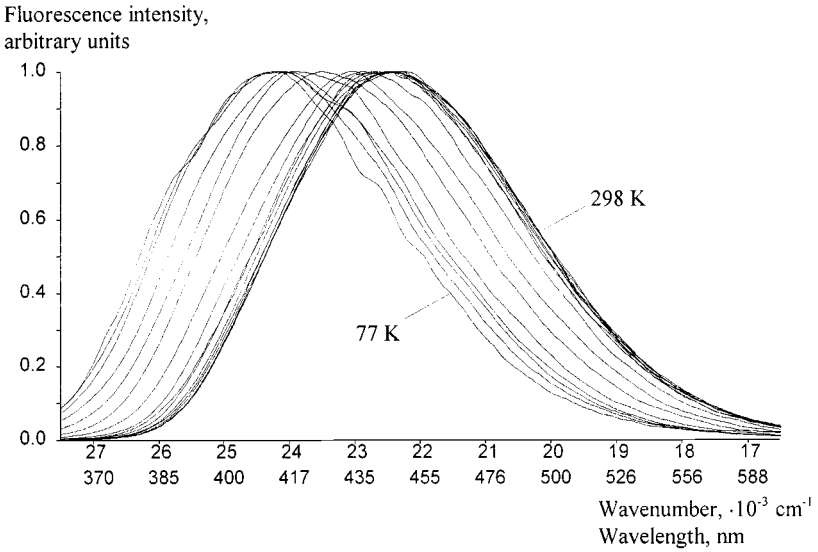

Fig. 3. Low temperature fluorescence spectra of *ortho*-POPOP in propanol-1 at the following temperatures: 298, 263, 253, 233, 223, 213, 183, 173, 163, 153, 143, 133, 123, 113 and 77 K.

of *ortho*-POPOP molecule [18], remain nearly the same as in liquid solutions at room temperature. In accordance with the conclusions of [18], this fact can be attributed to the peculiar fixing of non-planar asymmetric conformation of *ortho*-POPOP molecule in glassy propanol-1 at low temperatures.

The abnormally high fluorescence Stokes shift, typical for the *ortho*-analogues of POPOP, was interpreted in our previous papers [18–20] in terms of excited state flattening of the studied molecules. Such an assumption was made on the base of comparison of the absorption and emission spectra of *ortho*-POPOP with those of its planar model compounds—2,5-diphenyl-oxazole (PPO) and 1,4-bis-(5-phenyl-oxazolyl-2)-benzene (POPOP) [18,20]. Indeed, the *ortho*-POPOP molecule has the energy of the long-wavelength transition in the absorption spectrum close to that of PPO, while as its fluorescence spectrum lies in the emission region of POPOP. Thus, we assumed that the excited state flattening results in partial restoration of conjugation between the two above discussed chromophoric fragments of the molecule of *ortho*-POPOP. This leads to the decrease of the energy of the fluorescent state, and, correspondingly, to the increase of the Stokes shift. However, until the present moment, no more or less direct experimental evidence in favor of this statement was presented yet.

The low temperature fluorescence spectra of *ortho*-POPOP, measured at the conditions analogous to the above-discussed absorption spectra, are shown in Fig. 3. Here we would like to note that very low solvatofluorochromic effects are typical to the unsubstituted molecule of ortho-POPOP in solvents of different polarity and proton donor ability [18–20]. Thus any deviations in fluorescence properties at low temperature may be connected mainly with the changes of molecular geometry.

It is clearly seen, that the emission band of *ortho*-POPOP shifts to the blue spectral region with the decreasing of temperature. The maximal blue shift, which was reached at liquid nitrogen temperature, was found to be near 2000–2500 cm^{-1}. If we subtract this value from the observed for the room temperature Stokes shifts and also take into acount definite red shift of long-wavelength absorption band, we would obtain "nearly normal" values of 4500–5500 cm^{-1}. The sigmoid-like dependence of the position of emission maxima on temperature has its inflection point near the melting point of the solvent used (146K). Thus, the excited state structural relaxation process of the *ortho*-analogues of POPOP can be considerably "freezed down" in glassy solvents at low temperature (it is interesting to note, that abnormally high fluorescence Stokes shifts are typical to the studied compound in polymer media, expressing the presence of particular free volume in the examined polymers). The above facts also indicate, that the structural relaxation of the *ortho*-POPOP molecule is connected with the high-amplitude intramolecular motion, which can be stopped only in solidified solutions. The position of the fluorescence band of *ortho*-POPOP at 77K is closer to that of PPO, rather than to that of POPOP at room temperature. Analyzing all the facts, we can conclude, that they correspond to our model of the excited state flattening of the molecule of *ortho*-POPOP.

To elucidate the degree of such flattening we made calculations of the investigated molecule with the optimi-

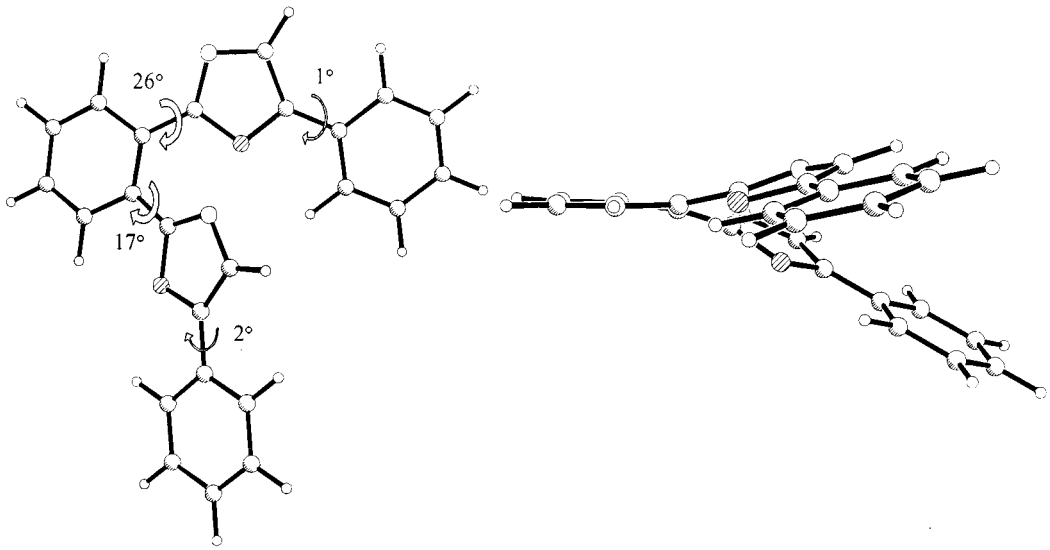

Fig. 4. Flattened structure of *ortho*-POPOP molecule in S_1^*-state. See legend to Fig. 1.

zation of its geometry in the lowest singlet excited state by the AM1 method. The resulting molecular structure is presented in Fig. 4. We would like to note, that definite excited state flattening is typical to both oxazole cycles of the investigated molecule. One of them, which was initially more coplanar with the central phenylene moiety, rotates by a small angle, about 3°, towards a more flatten structure. However, as it could be expected, the most considerable changes occur in the other fragment. The initially out-of-plane oxazole cycle rotates by the angle of nearly 40° around the single bond, which connects it with the central phenylene ring.

These intramolecular rotations must result in a considerable increase of sterical hindrance in the excited molecule of *ortho*-POPOP. However, the increasing strain is partially relieved by the distortion of planarity of the central phenylene nucleus: mean deviation of its atoms from the "least square" plane increases from 0.004 A in the ground state to 0.054 A in the excited state. Moreover, in the relaxed excited molecule of *ortho*-POPOP the dihedral angle between the bonds, which connect the central phenylene nucleus to the heterocycles, was found to increase to 24° from ~3° in the ground state. Thus, the molecule of *ortho*-POPOP become considerably more flatten and also a little more symmetric in the excited state, compared to the ground state. The gain in energy due to the formation of flattened structure in the lowest singlet excited state, estimated by AM1 method (difference in energy between the excited Franc-Condon state, which correspond to the optimal ground state geometry and the excited state optimized molecular conformation), was found to be near 2900 cm^{-1}, expressing the noticeable driving force of the excited state structural relaxation (Fig. 5). Let us note that much better correspondence between the calculated and the experimental excited states energies could be obtained by any of the specially parameterized semiempirical methods, for example, CNDO/S (see discussion below).

It was interesting to find out how the non-planarity of molecules and the excited state partial flattening influence the fluorescence properties of the *ortho*-analogues of POPOP. It is well known that disruption of planarity in many cases may result in the decreasing of the emission quantum yield of conjugated organic compounds. For this purpose, we made CNDO/S CI calculations of both initial and flattened conformations of *ortho*-POPOP, trying also to evaluate spin-orbit coupling of their lowest singlet excited state with all the lower-lying triplet levels. The correspondent results are presented in Table I. The expected increase in the probability of intersystem crossing was found for the initial non-planar molecule of *ortho*-POPOP. According to our estimation with the use of the rate constants of primary photophysical processes, which are listed in Table I, the fluorescence quantum yield at the absence of structural relaxation ($\varphi' = k^f/(k^f + k^{ISC})$) must not exceed 0.44. The analogous evaluation for the hypothetical flatten structure gives its hypothetical quantum yield value near 0.99.

The total fluorescence quantum yield of *ortho*-POPOP may be evaluated, basing on the proposed and

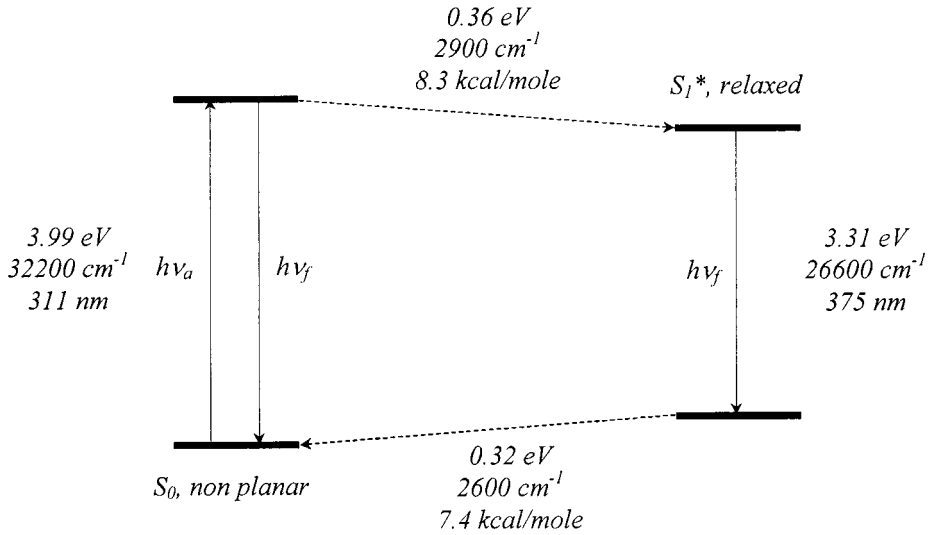

Fig. 5. Four-level energetic diagram, obtained by the AM1 calculations with the optimization of molecular geometry in the ground ("S_0, non planar"; see Fig. 1) and in the excited state ("S_1^*, *relaxed*"; see Fig. 4). Two other energetic levels correspond to the Franc-Condon states, calculated for the above-mentioned optimized geometries.

Table I. Calculated Spectral and Photophysical Parameters, Spin-Orbit Coupling of the Fluorescent State for the Initial Non-Planar and Flattened Conformations of *ortho*-POPOP with All the Lower Lying Triplet States[a]

Level	E (eV)	λ (nm)	ν (cm^{-1})	f	k_f (s^{-1})	Level	E (eV)	λ (nm)	ν (cm^{-1})	β_{ij} (cm^{-1})	k^{ISC} (s^{-1})
					Initial non-planar confirmation (Fig. 1)						
S_1	3.49	356	28,130	0.33	$3.9\cdot10^8$	T_3	3.37	368	27,210	0.277	$4.9\cdot10^8$
						T_2	2.56	484	20,670	0.156	$1.6\cdot10^5$
						T_1	2.47	502	19,920	0.167	$1.2\cdot10^5$
Total											$4.9\cdot10^8$
					Structurally relaxed flattened conformation (Fig. 4)						
S_1	2.72	456	21,930	0.41	$3.0\cdot10^8$	T_2	2.16	575	17,380	0.155	$1.5\cdot10^6$
						T_1	1.91	650	15,370	0.101	$1.3\cdot10^5$
Total											$1.6\cdot10^6$

[a] E—the energies of singlet and triplet excited states; λ and ν—wavelength and wavenumber of calculated electronic transitions; f—oscillator strength for the long-wavelength transition in the electronic absorption spectra: k_f—fluorescence radiative rate constant; β_{ij}—values of the matrix elements of the operator of spin-orbit coupling of S_1^*-state with the correspondent lower lying triplet levels; k_{ISC}—radiationless rate constant for intersystem crossing, evaluated according to Robinson and Frosch [26].

grounded by us in [18] discrete model of the excited state structural relaxation process in this molecule. Our estimation of the rate constant of the excited state flattening, which was determined to be near $3.7\cdot10^8$ s^{-1}[18], must be also taken into account. Thus, for the conditions of photostationarity, one can obtain the following equation (here NP denotes the initial non planar structure, EF—excited state flattened conformation, Rel—relaxation process, k^f—radiative rate constant, k^{ISC}—intersystem crossing rate constant):

$$\varphi_\Sigma = \varphi_{NP} + \varphi_{Rel} \cdot \varphi_{EF} = \frac{k^f_{NP}}{k^f_{NP} + k_{Rel} + k^{isc}_{NP}} + \frac{k_{Rel}}{k^f_{NP} + k_{Rel} + k^{isc}_{NP}} \cdot \frac{k^f_{EF}}{k^f_{EF} + k^{isc}_{EF}}$$

The resulting theoretical value $\varphi_\Sigma = 0.61$ is close within the experimental error to the experimental data, obtained by us earlier [18,20] for various solvents at room temperature (for example, 0.55 for octane and 0.57 for propanol-2 [18]). Thus, the excited state structural relaxation manifests itself as a factor of increase of fluorescence quantum yield. The faster is the excited state flattening, the closer is the total quantum yield to the higher values typical to the flat aromatic oxazolic compounds (for example, 0.7-0.9 for PPO and POPOP). And, on the contrary, if the starting non-planar asymmetric structure would be fixed, the decrease of fluorescence efficiency down to the values of 0.3-0.5 might be predicted on the base of our calculations.

Summarizing, we can conclude that definite decrease of fluorescent efficiency caused by non-planarity is typical to *ortho*-analogues of POPOP. However, high fluorescence Stokes shifts of these molecules makes them more favorable from the point of total fluorescence losses, which can be even lower in most of their possible applications owing to the practical absence of overlap between the absorption and emission spectra.

CONCLUSION

Low temperature absorption and fluorescence spectra measurements, together with quantum chemical calculations with optimization of molecular geometry in the ground and in the lowest singlet excited states showed the considerable flattening of *ortho*-POPOP in the S_1*-state, which caused typical for it abnormally high fluorescence Stokes shift.

It was shown, that ground state non-planarity and the excited state flattening of the *ortho*-analogues of POPOP do not result in significant increase of spin-orbit coupling, so fluorescence quantum yields of compounds, which belong to this class, must remain relatively high.

REFERENCES

1. F. Vollmer, W. Rettig, and F. Birkner (1994) *J. Fluoresc.* **4**, 65–69.
2. C. Zorn, M. Bowen, S. Majewski, J. Walkr, R. Wojcik, C. Hurlbut, and W. Moser (1988) *Nucl. Instrum. Methods Phys. Rev. A* **271**(3), 701–703.
3. V. M. Feygelman, J. K. Walker, A. R. Katritzky, and Z. Dega-Szafran (1989) *Chem. Scripta* **29**, 241–243.
4. W. Klopffer (1977) *Adv. Photochem.* **10**, 311–358.
5. U. Yu. Martynov, A. B. Demyashkevich, B. M. Uzhinov, and M. G. Kuzmin (1977) *Russ. Chem. Rev.* **46**, 1–31.
6. M. Kasha (1986) *J. Chem. Soc. Faraday Trans. 2* **82**, 2379–2392.

7. S. J. Formosinho and L. G. Arnaut (1993) *J. Photochem. Photobiol. A Chem.* **75**, 21–48.
8. S. M. Ormson and R. G. Brown (1994) *Progr. React. Kinet.* **19**, 45–91.
9. D. Le Gourrierec, S. M. Ormson, and R. G. Brown (1994) *Progr. React. Kinet.* **19**, 211–275.
10. A. Douhal, F. Lahmani, and A. H. Zewail (1996) *Chem. Phys.* **207**, 477–498.
11. E. Lippert (1961) *Lum. Org. Inorg. Mater. Int. Conf., New York*, pp. 271–273.
12. K. Rotkiewicz, Z. R. Grabowski, A. Krowczynski, and W. Kunhle (1976) *J. Luminesc.* **12/13**, 877–885.
13. A. Siemiarczuk, Z. R. Grabowski, A. Krowczynski, M. Asher, and M. Ottolenghi (1977) *Chem. Phys. Lett.* **51**, 315–320.
14. Z. R. Grabowski, K. Rotkiewicz, A. Siemiarczuk, D. J. Cowley, and W. Baumann (1979) *Nouv. J. Chim.* **3**, 443–454.
15. W. Rettig (1986) *Angew. Chem.* **98**, 969–986.
16. A. O. Doroshenko, L. D. Patsenker, V. N. Baumer, L. V. Chepeleva, A. V. Vankevich, O. P. Shilo, S. N. Yarmolenko, V. M. Scherschukov, V. G. Mitina, and O. A. Ponomaryov (1994) *Zhurn. Obsch. Khim.* **64**, 646–652 (in Russian).
17. A. O. Doroshenko, L. D. Patsenker, V. N. Baumer, L. V. Chepeleva, A. V. Van'kevich, A. V. Kirichenko, S. N. Yarmolenko, V. M. Scherschukov, V. G. Mitina, and O. A. Ponomaryov (1994) *Mol. Eng.* **3**, 353–363.
18. A. O. Doroshenko, A. V. Kirichenko, V. G. Mitina, and O. A. Ponomaryov (1996) *J. Photochem. Photobiol. A Chem.* **94**, 15–26.
19. A. O. Doroshenko, V. N. Baumer, A. V. Kirichenko, V. M. Scherschukov, and A. V. Tolmachev (1997) *Khim. Heterocycl. Soed.*, 1549–1558 (in Russian).
20. A. V. Kirichenko, A. O. Doroshenko, and V. M. Scherschukov (1998) *Chem. Phys. Reports* **17**, 1643–1651.
21. J. Jasny (1978) *J. Luminesc.* **17**, 149–173.
22. M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, and J. J. Stewart (1985) *J. Am. Chem. Soc.* **107**, 3902–3909.
23. J. Del Bene and H. H. Jaffe (1968) *J. Chem. Phys.* **48**, 1807–1813.
24. K. Nishimoto and N. Mataga (1957) *Z. Phys. Chem. (Frankfurt am Main)* **13**, 140–151.
25. Yu. F. Pedash, V. E. Umansky, and O. A. Ponomarev (1997) *Funct. Mater.* **4**, 138–144.
26. G. W. Robinson and R. P. Frosch (1963) *J. Chem. Phys.* **38**, 1187–1203.