Nature of 2-Aminoxanthone Fluorescence

V. G. Syromyatnikov,[1] V. M.(N.) Yashchuk,[2,4] T. Yu. Ogul'chansky,[2] O. O. Novikova,[1] Yu. P. Piryatinsky,[3] and O. Yu. Kolendo[1]

Absorption and fluorescence spectra of 2-aminoxanthone in solutions of different types at 77–350 K were studied. The existence of three bands ($\lambda_{1\,max} = 417$ nm, $\tau_1 = 14$ ns; $\lambda_{2\,max} = 528$ nm, $\tau_2 = 13$ ns; and $\lambda_{3\,max} = 565$ nm, $\tau_3 = 6$ ns) in fluorescence of 2-aminoxanthone solutions has been established. It was shown that the first short-wave band was determined by deactivation of singlet excitation of an aminoxanthone molecule. The band with $\lambda_{3\,max} = 565$ nm (depending on the concentration) is connected with excimer-type aggregates, which are formed by aminoxanthone molecules grouped with the help of dipole molecules of solvent or by weak hydrogen bonds between aminoxanthone molecules. The emission in band $\lambda_{2\,max} = 528$ nm is caused by reversible changes in the 2-aminoxanthone molecule and probably is connected with an intramolecular proton transfer.

INTRODUCTION

Lately the photophysics and photochemistry of xanthone and its derivatives have been the object of a number of works due to their important role in phytochemistry, pharmacy, pharmacology, and other fields [1–4]. The fluorescence from a modification of xanthone is also interesting due to numerous applications of xanthone derivatives [3,4], particularly in information recording ("stereolithography")[5] and nonlinear optics (for example, in Ref. 6 a molecular and crystal susceptibilities of 3-aminoxanthone as a new second-harmonic generation material were theoretically studied).

The photophysical properties of xanthone molecules are determined mainly by the individual properties of their π-electron systems. Absorption and luminescence spectra of xanthone are presented in Ref. 7 and are connected with transitions between correspondent energy levels. On the contrary, the fluorescence spectra of 2-aminoxanthone are rather complicated. Their spectral intensity distribution depends to a great extent on the temperature, type of solvent, and concentration. As far as we know, the nature of 2-aminoxanthone fluorescence has not been examined before. In the present paper an attempt to determine the nature of 2-aminoxanthone fluorescence has been made.

EXPERIMENTAL

2-Aminoxanthone was synthesized by way of reduction of nitroxanthone followed by nitration of xanthone [8,9] and was crystallized from CH_3OH (mp, 196–197°C). The solvents were purified according to the instructions given in Ref. 10. Experiments were carried out in the temperature range 77–350 K. A nitrogen pulse laser with a wavelength of emission 337 nm and a Hg lamp with a set of optical filters were used as sources of excitation. The absorption spectra were recorded with a Specord UV VIS spectrophotometer, and the lumines-

[1] Chemical Department, Kyiv National Taras Shevchenko University, Volodymyrska St. 64, 252033 Kyiv, Ukraine.
[2] Physics Department, Kyiv National Taras Shevchenko University, Academica Glushkova St. 6, 252022 Kyiv, Ukraine.
[3] Institute of Physics NASU, Prospect Nauki 46, 252028, Kyiv, Ukraine.
[4] To whom correspondence should be addressed.

cence was studied using a spectrometer for steady-state luminescence measurements designed in our laboratory.

A nanosecond gate laser set [11] was used for fluorescence decay measurements. The detection system was based on a pulse high-speed recording photomultiplier ELU-FTS (manufacture of the USSR). The resolution time of the system was ~0.1 ns (taking into account the method of calculations).

The software packages Mopac and HyperChem 5.0 of the Institute for Organic Chemistry, Ukrainian Academy of Sciences, were used for the calculations and for generating figures. Geometry optimization for the ground and excited states of 2-aminoxanthone molecule was realized by the semiempirical PM3/CI level of theory (software package Mopac). EF methods were used for gradient normalization. Further, maps of the electron density distribution on the lower vacant and upper occupied molecular orbitals of the 2-aminoxanthone molecule were made using the software package HyperChem 5.0.

RESULTS AND DISCUSSION

Absorption

Absorption spectra of 2-aminoxanthone solutions in ethanol and dioxane are presented in Fig. 1. The shape of these spectra does not depend on the concentration of 2-aminoxanthone solutions in the range 10^{-2}–10^{-6} M. That proves the molecular character of absorption. On the other hand, the structure of the 2-aminoxanthone

absorption spectra is near that of the xanthone spectra but a long-wave spectral shift is observed compared to xanthone [7]. Such spectral behavior of 2-aminoxanthone absorption is connected with the fact that mainly the xanthone π-electron system perturbed by a NH_2- group is responsible for absorption of 2-aminoxanthone molecules.

Fluorescence

Three practically unstructured bands are observed for fluorescence of 2-aminoxanthone at 293 K (contrary to xanthone, for which only one fluorescence band is observed according to our measurements): $\lambda_{1\,max} = 417$ nm, $\lambda_{2\,max} = 528$ nm, and $\lambda_{3\,max} = 565$ nm (Fig. 1). Corresponding decay times (τ) are $\tau_1 = 14$ ns, $\tau_2 = 13$ ns, and $\tau_3 = 6$ ns. Decay curves for all fluorescence bands are presented in Fig. 2. As follows from it, the rise times for all emission bands are close. This fact testifies to the similar nature of primary excited centers. The behavior of fluorescence bands is rather different with respect to the varying conditions.

The shape of the most short-wave band of 2-aminoxanthone fluorescence (band I) with maximum $\lambda_{1\,max} = 417$ nm (which is observed over a wide range of temperatures and for different types of solvents) and the shape of the first long-wave absorption band correspond to the mirror image rule (Fig. 1). Decay of emission in this band is single exponential, $\tau_1 = 14$ ns. This fluorescence band is similar to the corresponding band of xanthone fluorescence and we believe that it is determined by the direct
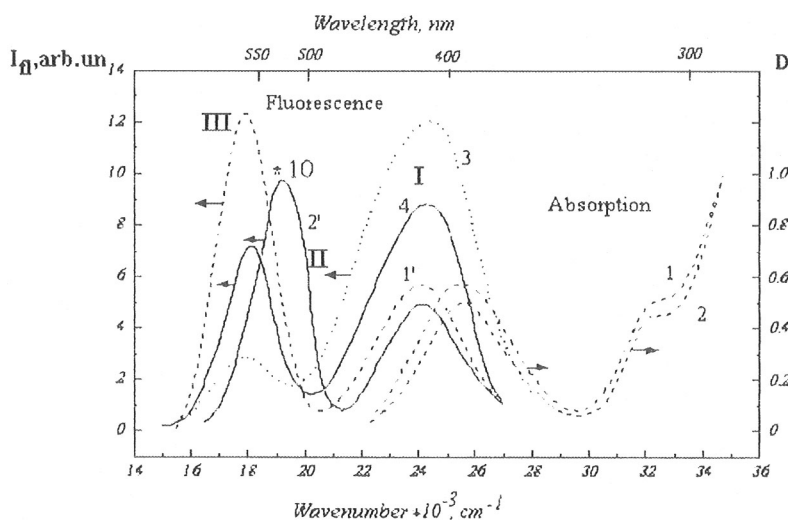
Fig. 1. Absorption (1, 2) and fluorescence (1', 2', 3, 4) spectra of 2-aminoxanthone. Solutions in dioxane (2, 2') and ethanol (1, 1', 3, 4). Concentration: 1, 2, 1', and 2'—10^{-4} M; 3—10^{-6} M; 4—10^{-5} M. T = 293 K.
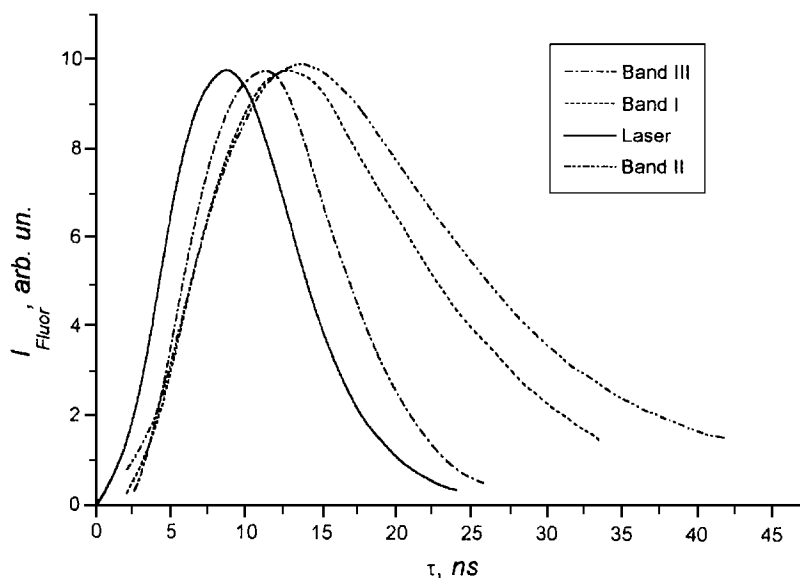
Fig. 2. Decay curves for bands of 2-aminoxanthone fluorescence.

deactivation of singlet excitation of the 2-aminoxanthone molecule.

The behavior of the band with maximum $\lambda_{3\,max} = 565$ nm (band III) is very complex. This band is observed simultaneously with band I (Fig. 1) in fluorescence spectra of ethanol solutions of 2-aminoxanthone at 373–180 K. We do not observe this band in fluorescence spectra at 77 K. The ratio of band III's intensity to the intensity of band I considerably depends on the concentration of the solution. As follows from Fig. 1, relative intensity of band III increases with an increase in concentration from $C = 10^{-6}\,M$. At $C = 10^{-4}\,M$ this band becomes dominating. The temperature dependence of band III intensity has a bell shape, with the maximum at 200–205 K (Fig. 3B).

Some facts testify to the possible excimer nature of emission centers that are responsible for fluorescence band III. They are (a) the absence of a corresponding band to band III in absorption spectra; (b) the increase in the ratio I_{III}/I_{I} (where I_{III} is the intensity of band III, and I_{I} the intensity of band 1) with an increase in the concentration; and (c) the character of the temperature dependence of fluorescence intensity. However, the half-width of band III ($\sim 2200\,cm^{-1}$) is less than the half-width of the monomer band ($\sim 4800\,cm^{-1}$), and, in addition, $\tau_3 < \tau_1$. That is not typical for "classic" excimers [12] but for excimer-like aggregates of dynamic type more than two species [13]. It is interesting that these aggregates are observed already at a quite low concentration ($C = 10^{-6}\,M$) This also is not typical for "classic" excimers. From our point of view, the formation of preag-gregate states (preaggregates) takes place in 2-aminoxanthone solutions. There are two variants of their structure: (a) a few 2-aminoxanthone molecules are grouped by weak hydrogen bonds as shown in Fig. 4A; and (b) preaggregates are created with the help of polar molecules of solvent (Fig. 4B). These preliminary groupings possess a configuration (distance between π-electron systems, degree of their overlapping) such that interaction between aminoxanthone π-electron systems is rather weak. That is why we did not observe significant changes in the corresponding absorption spectra. We interpret our band III data in such a way that photoexcitation and simultaneous activation lead to the formation of bound exciting states of aggregates (dynamic aggregates), the deactivation of which causes emission in the spectral region corresponding to band III. A similar effect for antraquinone dyes was observed in Ref. 13.

Band II ($\lambda_{2\,max} = 528$ mm) appears in fluorescence spectra of aminoxanthone in nonpolar solutions (Fig. 1). The behavior of band II is essentially different from that of band III under varying conditions (concentration, temperature). The ratio of intensities I_{II}/I_{I} depends weakly on the concentration. On the other hand, the relative intensity of band II does not decrease with decreasing temperature. So there is no reason to suppose that fluorescence center II is a static or dynamic complex or aggregate. Thus it is natural to suppose that the center which is responsible for band II is created as a result of some intramolecular process initiated by photon absorption. The conclusion could be made that transformation of the aminoxanthone excited molecule is connected with the
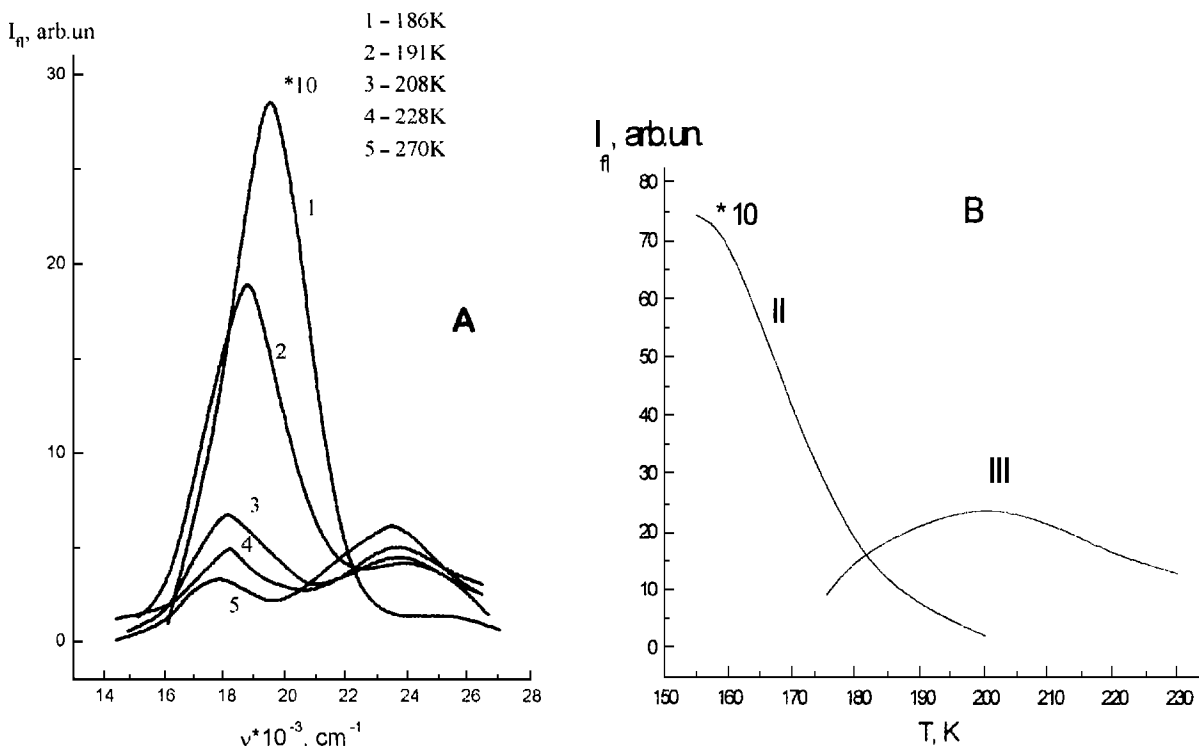
Fig. 3. (A) Fluorescence spectra of 2-aminoxanthone at different temperatures. Ethanol solutions, $C = 0.5 * 10^{-4}$ M. (B) Temperature dependence of band II and III fluorescence intensity.

presence of the amino group, taking into account the abscence of an analogous band in fluorescence spectra of xanthone. Computer calculation of the distribution of aminoxanthone's electron charge the density in the ground and excited states by semiempirical method PM3 shows that excitation of aminoxanthone molecules (first excited level) leads to a redistribution of electron density. A significant transfer of charge density takes place (Fig. 5). Such a variation of charge density could stimulate proton transfer from the amino group to oxygen (in the xanthone system) (Fig. 6). It is known [14] that the radiation deactivation of such an excited state leads to the appearance of an unstructured long-wave (in comparison with the band that is analogous to band I) band in the fluorescence spectrum. From a comparison of the temperature dependencies for band II and band III (Fig. 3B), one can conclude that in polar solutions the process of proton transfer is blocked by the dynamic aggregate formation after photon absorption. In the temperature range $T < 180$ K, where dynamic aggregates are not formed, the process of proton transfer takes place in polar solutions as well. This is the reason for the band II domination in 2-aminoxanthone fluorescence spectra under these conditions. It is important to note that we have observed the domination of band II in flourescence spectra of 2-amino-

xanthone films and powders as well as in different quite nonpolar polymer matrixes such as polyvinylethylal and polyvinylbutyral. In our opinion, this suggests the possibility that the specific interactions between dioxane and 2-aminoxanthone do not have an essential influence on the processes mentioned above.

The facts presented above also testify to the formation of preaggregate states with the help of polar solvent molecules as shown in Fig. 4B. However, for a more complete understanding of the results obtained, additional studies are necessary, particularly with the application of high time-resolved spectroscopy (time resolution $\tau \sim 10^{-15}$ s).

CONCLUSIONS

1. Two long-wave bands ($\lambda_{2\,max} = 528$ nm, $\lambda_{3\,max} = 565$ nm) in fluorescence spectra of 2-aminoxanthone solutions (besides the short-wave band, $\lambda_{1\,max} = 417$ nm, that corresponds to the xanthone fluorescence band) are associated with the presence of the amino group.

2. The band with $\lambda_{max} = 565$ nm (which depends on the concentration) is connected with the emission of excimer-type aggregates that are formed by 2-aminoxan-
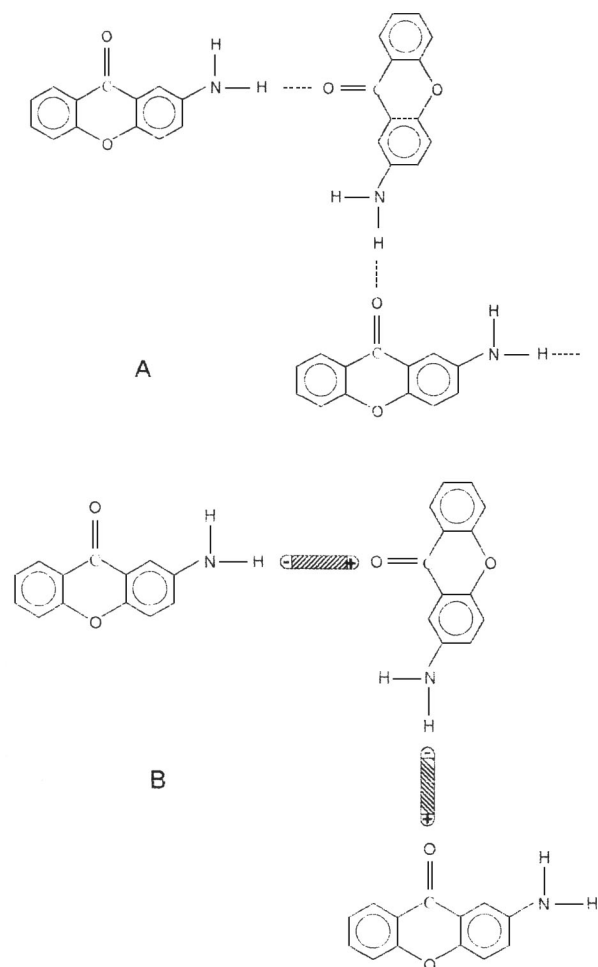
Fig. 4. Hypothetical variants of preaggregate structure: (A) by weak hydrogen bonds; (B) with the help of polar solvent molecules.
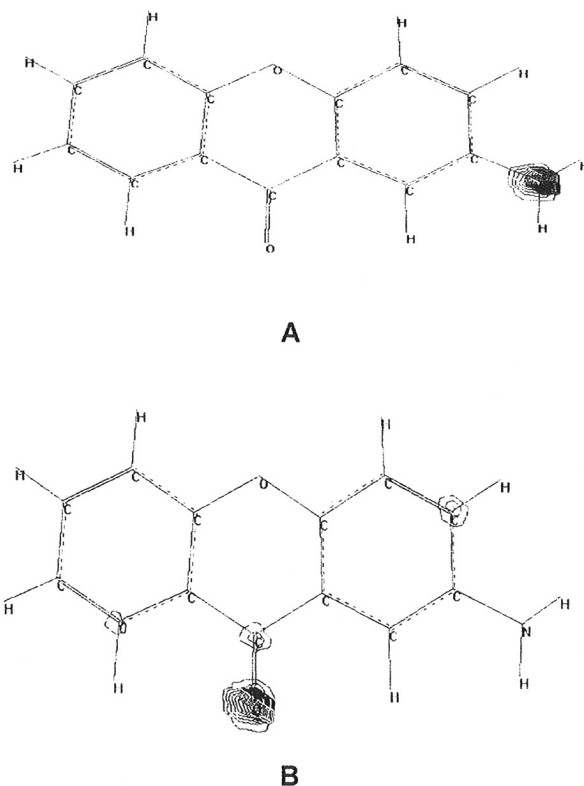

A

B

Fig. 5. Electron density on lower vacant (LUMO) (A) and upper occupied (HOMO) (B) molecular orbitals of the 2-aminoxanthone molecule.
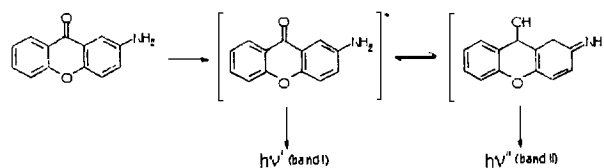

Fig. 6. Proposed scheme of proton transfer.

thone molecules previously grouped with the help of dipole molecules of solvent or by weak hydrogen bonds between 2-aminoxanthone molecules.

3. The band with λ_{max} = 528 nm observed in fluorescence spectra is associated with reversible changes in the electron system of the 2-aminoxanthone molecule after photon absorption. It is suggested that these changes are caused by intramolecular proton transfer.

ACKNOWLEDGMENTS

REFERENCES

1. L. J. Harrison, L. S. Leong, Y. W. Leong, G. L. Sia, K. Y. Sim, and H. T. W. Tan (1994) *Nat. Prod. Lett.* **5**, 111–116.
2. G. L. Sia, G. J. Bennett, L. J. Harrison, and K. Y. Sim (1995) *Phytochemistry* **38**, 1521–1528.
3. C.-N. Lin, M.-I. Chung, S.-J. Liou, *et al.* (1996) *J. Pharm. Pharmacol.* **48**(5), 532.
4. C.-N. Lin, S.-J. Liou, T.-H. Lee, *et al.* (1996) *J. Pharm. Pharmacol.* **48**(5), 539.
5. D. C. Neckers, S. Hassoon, and E. Klimtchuk (1996) *J. Photochem. Photobiol. A Chem.* **95**, 33–39.
6. T. Hamada (1996) *J. Phys. Chem.* **100**(50), 12, 19344–19349.
7. A. N. Anoshin, G. A. Valkova, E. A. Gastilovich, *et al.* (1984) *Vibronic Spectra of Aromatic Compounds with Heteroatoms*, Nauka, Moscow, p. 182 [in Russian].

8. Hamano Kijosi and Kogyo Kagaku Zasshi (1968) *J. Chem. Soc. Japan Ind. Chem. Sect.* **71**, 463–464.

9. A. A. Goldberg and H. TA. Walker (1953) *J. Chem. Soc.* 1348–1357.

10. A. J. Gordon and R. A. Ford (1972) *The Chemist's Companion. A Handbook of Practical Data, Techniques, and References*, Wiley–Interscience, John Wiley and Sons, New Yor–London–Sydney–Toronto.

11. Yu. P. Piryatinsky, V. N. Yashcuk, Yu. A. Cherkasov, *et al.* (1990) *Zh. Prikl. Spectr.* **53**, 41–48.

12. J. B. Birks (1975) *Rep. Prog. Phys.* **38**, 903–974.

13. Yu. P. Piryatinsky, V. N. Yashchuk, and O. V. Yatsun (1995) *Funct. Mater.* **2**(1), 127–131.

14. V. G. Pivovarenko, A. D. Roshal, and A. P. Demchenko (1996) in *XVII IUPAC Symposium on Photochemistry*, Helsinki, p. 489.