Fluorescence Spectra of Acridine-Mercuric Halide Complexes

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It has been reported that acridine is non-fluorescent in the solid state and in nonpolar solvents such as hexane and benzene.[1] In polar solvents such as alcohol and water capable of forming hydrogen bonds, acridine emits a blue fluorescence.[1,2] The radiationless deactivation of an excited molecule of acridine has been ascribed to interaction between n- and π-electrons.[2] In polar solvents, an excited molecule of acridine combines rapidly with the nearest OH group of a solvent molecule. Such a hydrogen-bonded molecule may be considered to be a fluorescent species, since the formation of hydrogen bonds in the excited state results in a decrease in the $n-\pi$ interaction.[1,2] Acridinium ions emit a green fluorescence in various solvents[1] as well as in the solid state. This fact also supports the interpretation that the non-radiative degradation of acridine in the excited state is due to the $n-\pi$ interaction.

Matsushita[3] examined the emission spectra of a number of benzylideneamine and salicylideneamine derivatives. He showed that the formation of intramolecular hydrogen bonds intensifies the emissivity of fluorescence because of the diminution of the n-electron contributions to the non-radiative degradation of the excited state.

Acridine forms crystalline molecular complexes with some inorganic compounds.[4] If the n-electrons at the nitrogen atom of acridine are involved in the formation of these molecular complexes, it is to be expected that the $n-\pi$ interaction in the excited state will be reduced to a great extent and that the fluorescence emission will be enhanced.

Experimental

Materials.—Acridine and mercuric halides were purified by sublimation or recrystallization. An acetone solution of acridine was added to an acetone solution of an appropriate mercuric halide in order to prepare the molecular complexes.

Fluorescence Measurements.—The fluorescence spectra of the molecular complexes were recorded with a Shimadzu model SV-50 AL spectrophotometer equipped with an accessory for measuring the fluorescence spectra of solid samples.

Results and Discussion

Acridine-mercuric halide (1 : 1) complexes emit a green fluorescence in the solid state. Table I shows the results obtained under illumination with

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[1] E. J. Bowen, N. J. Holder and G. B. Woodger, *J. Phys. Chem.*, **66**, 2491 (1962).

[2] N. Mataga and S. Tsuno, This Bulletin, **30**, 368 (1957).

[3] S. Matsushita, *J. Chem. Soc. Japan, Pure Chem. Sect. (Nippon Kagaku Zasshi)*, **84**, 373 (1963).

[4] a) H. Buss, H. W. Kohlschuetter and D. Maulbecker, *Z. Naturforsch.*, **18b**, 417 (1963); b) W. Ludwig and G. Wittmann, *Helv. Chim. Acta*, **47**, 1265 (1964).

TABLE I. FLUORESCENCE SPECTRA AND PHOTOCONDUCTIVITIES OF ACRIDINE-MERCURIC HALIDE COMPLEXES

Compound	Emission max., mμ*	Relative intensity	Photo-conductivity	Analysis N	
				Calcd.	Obsd.
Acridine·HCl	491, 512(s)	100, 86	—	—	—
Acridine·$HgCl_2$	505	50	—	3.11	3.27
Acridine·$HgBr_2$	492	20	—	2.60	2.59
Acridine·HgI_2	500	2	—	2.21	2.35

* Corrections due to photomultiplier sensitivity were not carried out. (s) means a "shoulder."

a light of $\lambda=350$ mμ. It should be noted that the intensity of emission depends markedly on the kind of halogen ions, while fluorescence maxima are located at nearly the same wavelengths. The small variation in the peak position is probably due to a small change in the interaction between acridine and mercuric halides. The decrease in the fluorescence intensity of complexes with the increase in the atomic weight of the halogen ions may be attributed to the spin-orbit coupling which is generally considered to be a mechanism promoting the radiationless deactivation of excited molecules.

It is of interest, in this connection, to note that mercury atoms, in spite of their heavy atomic weight, do not strongly promote the spin-orbit coupling in diminishing the emission. This fact suggests that the mercury atoms may be located in the molecular plane of acridine, because the π-orbitals have their nodal planes on the molecular plane of acridine and, therefore, the spin-orbit interaction might be small. As judged from the efficiency of the spin-orbit coupling of the halogen ions, the mercuric halide molecules may be oriented perpendicular to the molecular plane of acridine, and the spin-orbit coupling between the nearest neighbor complex molecules may contribute to the diminution of emission. The square planar configuration about the metal atom was pointed out for NiI_2-(Acridine)$_2$ in the solid state.[4b]

The present authors examined the absorption spectra of two kinds of films of acridine-mercuric halides, one of which was prepared by the sublimation of an appropriate mercuric halide onto a presublimated film of acridine, while the other was prepared by the sublimation of acridine-mercuric halide complexes. The latter gave better results except for the case of acridine-mercuric iodide. Acridine hydrochloride yielded no good results, probably because it decomposes by losing hydrogen chloride. These complexes show broad absorption bands very similar to those of acridinium cations in solution with structures over the range of 350—440 mμ. From the similarity observed in the absorption and the fluorescence spectra, it may be considered that the electronic structure of the acridine part in the complexes is essentially the same as that of the acridinium cation. Thus, it may be concluded that the *n*-electrons at the nitrogen atom of acridine are partially transferred to the mercury atom, affording an intermolecular binding force.

Good photoconductive materials can be found among luminescent species.[5] In fact, anthracene is a representative photoconductive material in organic compounds, whereas acridine shows no good photoconductive property. From this point of view, the photoconductivity of these complexes was measured in a surface cell consisting of a polycrystalline pellet pressed under 1 kbar and two gold electrodes spattered onto the same surface of the pellet with a narrow gap of 1 mm. No positive results were obtained. In aromatic hydrocarbons, the photocarrier generation process in the crystal absorption region has been discussed in terms of the dissociation of singlet excitons on the crystal surface, but the idea that the photocarrier generation originates in exciton-exciton annihilation can not be eliminated.[6] In any case, the energy transfer of excitons produced by light absorption is essentially required for generating carriers. In the present case, acridine molecules seem to be separated from one another by intervening mercuric halide molecules. This weakens the overlap between the π-orbitals of the nearest neighbor acridine molecules to the extent that the exciton transfer is impossible. Therefore, no photocurrents were observed.

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5) M. Kleinerman, L. Azarraga and S. P. McGlnny, *J. Chem. Phys.*, **37**, 1825 (1962).

6) P. J. Reucroft, O. N. Rudyj, R. E. Salomon and M. M. Labes, ibid., **43**, 767 (1965), and references therein.