Physical Chemistry

R. N. Nurmukhametov, Yu. I. Kozlov, D. N. Shigorin, and V. A. Puchkov

1962

SovietRxiv

Abstract

Full Text

Physical Chemistry

R. N. Nurmukhametov, Yu. I. Kozlov, D. N. Shigorin, and V. A. Puchkov

Luminescence Spectra of Azomethine Compounds

(Presented by Academician A. N. Terenin, 23 X 1961)

In work (1) it was shown that oxyazo compounds exhibit fluorescent ability when an intra- or intermolecular H-bond arises, leading to strengthening of the molecular system in which the $n \to \pi^*$ transition in the azo group ($—N=N—$) is responsible for electronic excitation.

The aim of the present work was to elucidate the intramolecular interactions favorable to the appearance of fluorescence in azomethine compounds. The luminescence spectra were investigated in powders and in n-hexane solutions ($C \sim 10^{-4}$ mol/l) at 293 and 77° K. The method used for recording the spectra is described in work (1). All azomethine derivatives were synthesized by us under standard conditions by heating equimolecular quantities of an aromatic aldehyde and an amine in propyl alcohol at the boiling temperature of the reaction mixture, except for salicylidene-β-aminoanthraquinone, which was obtained from salicylaldehyde and β-aminoanthraquinone in boiling cyclohexanol. To obtain pure preparations, the azomethines were dissolved in chloroform and chromatographed on Al_2O_3, after which they were crystallized from a suitable solvent (alcohols $C_1—C_4$, benzene, chlorobenzene).

We investigated the following azomethines of general formula A for luminescence:

[structural formula A]

(indicated are the serial number of the compound, the position and character of the substituent, and the melting point in °C):

No.	Substituents	Melting point, °C	No.	Substituents	Melting point, °C
I	$R = R' = H$	47.5–48.5°	II	$R =$ o-OH$R' =$ H	52–53°
III	$R =$ n-OH$R' =$ H	188.2–189.2°	IV	$R =$ o-$OCH_3$$R' =$ H	41.0–42.5°

Fig. 1

Figure 1: Fig. 1

No.	Substituents	Melting point, °C	No.	Substituents	Melting point, °C
V	$R =$ H $R' =$ *o*-OH	91.0—91.5°	VI	$R =$ H $R' =$ *n*-OH	184—185°
VII	$R =$ H $R' =$ *n*-OCH_3	70.5—72°	VIII	$R =$ *o*-Cl $R' =$ *o*-OH	91—92°
IX	$R = R' =$ *o*-OH	183—184°	X	$R =$ *n*-$N(CH_3)_2$ $R' =$ H	100.5—101°
XI	$R =$ H $R' =$ *n*-$N(CH_3)_2$	89.0—90.5°	XII	$R =$ *n*-NO_2 $R' =$ H	89.0—89.5°
XIII	$R =$ *n*-NO_2 $R' =$ *n*-CH_3	123.9—124.7°	XIV	$R =$ *n*-NO_2 $R' =$ *n*-OH	169.2—170°
XV	$R =$ *n*-NO_2 $R' =$ *n*-OCH_3	134.7—135.2°			

as well as the compounds:

[structural formulas XVI and XVII]

XVI. ~ 45°

XVII. 76.5—77.5°

XVIII. 229-230.2°

XIX. 92.6-93.8°

Benzylideneaniline (I) exhibits no fluorescence either in powders or in solutions. Bright fluorescence appears upon introduction of an OH group into the ortho position of the aromatic ring bonded to the C atom of the azomethine group, or upon introduction of a $(CH_3)_2N$ group into any of the para positions. The *o*-hydroxy derivatives (compounds II, IX, XVI, XVII, XVIII, and XIX) and the *p*-dimethylamino derivatives of azomethines (compounds X and XI) possess fluorescence in powders at 293° and 77° K and in solutions frozen at 77° K. The para-hydroxy and para-methoxy derivatives of azomethines (III, VI, VII) exhibit no fluorescence. Methylation of the *o*-hydroxy group leads to disappearance of luminescence (IV). The para-nitro derivatives, as

Fig. 2

Figure 2: Fig. 2

Fig. 1

Fig. 2

Fig. 1. Fluorescence spectra of *o*-hydroxybenzalmesidine (XVI) at 77° K and excitation $\lambda_{\mathrm{Hg}} = 365$ mμ. 1 –in hexane solution before irradiation (×1), 2 –in hexane solution after irradiation (×0.8), 3 –powder before irradiation (×2), 4 –melt before irradiation (×1), 5 –powder after irradiation (×2), 6 –melt after irradiation (×1.6)

Fig. 2. Fluorescence spectra of *p*-derivatives of benzal aniline upon excitation $\lambda_{\mathrm{Hg}} = 365$ mμ. Fluorescence of benzal-*p*-dimethylaminoaniline (XI). 1 –powder at 77° K (×5), 2 –powder at 293° C (×20), 3 –in hexane at 77° K (XI). Fluorescence of *p*-dimethylaminobenzalaniline (X) at 77° K; 4 –powder before irradiation (×15), 5 –in hexane before irradiation at 77° K (×1), 6 –in hexane after irradiation at 77° K (×6), 7 –fluorescence of powder (XIII) of *p*-nitrobenzal-*p*-toluidine (×15)

a rule, do not fluoresce (XII, XIV, XV). An exception is compound XIII, which fluoresces in powder at 77° K.

It is of interest that, upon irradiation with ultraviolet light of powders and frozen solutions in *n*-hexane of *o*-hydroxybenzylideneaniline (II), *o*-hydroxybenzylidenemesidine (XVI), and *o*-hydroxybenzylidene-*α*-naphthylamine (XVII), a shift of the emission spectrum occurs with a simultaneous decrease in intensity. At the same time, a bathochromic change in the color of the samples and in the color of the luminescence is observed visually. The efficiency of the spectral changes depends on the wavelength of the irradiating light*.

Upon slight heating of the samples and subsequent cooling to 77° K, the color and emission spectrum acquire their original appearance. On going from the powder to the melt, a sharp increase in the intensity of luminescence occurs, while the emission curve of the melt remains the same as that of the powder. Reversible photochanges of the luminescence spectra also take place in the melt. Figure 1 serves as an illustration of the indicated effects; it shows the curves of the emission spectra of the powder, solution, and melt of *o*-oxybenzylidenemesidine (XVI) at 77° K before and after irradiation.

During the recording of the emission spectra before irradiation, phototransformation of the samples occurred, and therefore in reality we have a

---

* Upon irradiation with filtered light $\lambda_{\mathrm{Hg}} = 313$ and 365 mμ, rapid photoconversion of the *o*-hydroxy-substituted azomethines is observed, whereas upon irradiation with $\lambda_{\mathrm{Hg}} = 405$ mμ it is slow.

superposition of the spectra of irradiated and unirradiated molecules, the ratio of which is determined by the efficiency of the phototransformation. For *o*-oxybenzylideneaniline (II) the rate of transformation is so high that it is not possible to record the spectrum before irradiation. Visually, a rapid decrease in the brightness of the green fluorescence and the appearance of yellow luminescence of medium brightness are observed. In 2-oxynaphthylideneaniline (XIX) and *o*-oxybenzylidene-β-aminoanthraquinone (XVIII), the emission spectra before and after irradiation do not differ. In this case, for XIX a certain decrease in luminescence brightness upon irradiation with ultraviolet light is observed.

The appearance of fluorescence in the *o*-oxy derivatives of azomethines considered above is associated with the formation of a six-membered quasiaromatic ring by means of a hydrogen bond, which leads to an increase in the stability of the entire molecular system ([1,2]). The excited state of the molecule is apparently due to the $n \rightarrow \pi^*$ transition of the group –C=N–, as in the case of ortho-oxyazo compounds ([1]).

The fluorescent ability depends not only on the presence of an intramolecular H bond, but also on the geometrical configuration of the rings formed by this bond. When an oxy group is introduced into the *o*-position of the benzene ring bound to nitrogen, an H bond is formed, leading to the appearance of a five-membered ring in which the –C=N group is not included; in this case fluorescence is not observed—for example, benzal-*o*-aminophenol (V), *o*-chlorobenzal-*o*-aminophenol (VIII).

Probably, during the $n \rightarrow \pi^*$ transition, rupture of the five-membered ring formed by the H bond occurs, which is the principal reason for the loss of luminescent properties of the molecules in this case. It is interesting that *o*-oxybenzal-*o*-aminophenol, having two oxy groups in the ortho position to the –C=N group, fluoresces considerably more weakly and changes its spectrum more slowly under photoirradiation owing to competition between two types of H bond participating in the formation of six- and five-membered rings. The presence of an intramolecular H bond in ortho-oxy derivatives of azomethines and the difference in their nature depending on the position of the –OH group is also confirmed by IR spectra measured by T. S. Ryabchikova. The frequency of the stretching vibration of the HO group participating in the formation of an intramolecular hydrogen bond for benzylidene-*o*-aminophenol (V) (with a five-membered H ring) is 3350 cm^{-1} in the melt and 3450 cm^{-1} in CCl_4 (1:400), while for *o*-oxybenzylidenemesidine (XVI) (with a six-membered H ring) it lies near 2750 cm^{-1}.

The observed reversible changes in color and electronic spectra upon irradiation with light of a number of systems with strong hydrogen bonds can be explained by photo-transfer of the proton of the hydroxyl to the nitrogen atom. A phenomenon of this kind for systems with intermolecular hydrogen bonds had earlier been found from fluorescence spectra by A. N. Terenin and A. V. Shablya using 9-(*n*-oxyphenyl)-acridine as an example ([3]). The absence of spectral changes upon irradiation in 2-oxynaphthylideneaniline (XIX) and *o*-oxybenzylidene-β-aminoanthraquinone (XVIII) is probably associated with the impossibility of photo-transfer of the proton because of steric hindrance.

An interesting case of change in luminescence upon irradiation is presented by azomethines containing dimethyl- in the para- or para′-positions.

the amino group, for which proton transfer is impossible. The emission spectra of such compounds are shown in Fig. 2.

In powder form, benzyl-*p*-dimethylaminoaniline (XI) exhibits bright fluorescence, whereas *p*-dimethylaminobenzalaniline (X) glows weakly. In frozen solutions, the luminescence intensities of these compounds differ little.

In the present case, apparently, the cause of the change in the spectrum of X upon irradiation is the disruption of the planar structure of the molecule during excitation.

Received
23 X 1961

References

1. R. N. Nurmukhametov, D. N. Shigorin et al., *Optics and Spectroscopy*, 1961.
2. D. N. Shigorin, N. A. Shcheglova et al., *DAN*, **132**, 1372 (1960).
3. A. N. Terenin, A. V. Shablya, *Optics and Spectroscopy*, **10**, issue 5 (1961).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.