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### Emission Spectra of Isomeric Trifluorotoluidines

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Fluorescence and phosphorescence spectra of isomeric trifluorotoluidines ( $\text{CF}_3\text{C}_6\text{H}_4\text{NH}_2$ ) have been studied. The solution fluorescence at room temperature shows that the emission is maximum under neutral conditions and is reduced under acidic conditions. Under alkaline conditions, it gives an additional band on the longer wavelength due to the corresponding anions. At liquid nitrogen temperature, all the isomers show a strong phosphorescence in 450 nm region and relative quantum efficiencies of the two emissions vary in the three isomers.

CONSIDERABLE amount of work has been reported on the fluorescence spectra of aniline and its derivatives. Berlman<sup>1</sup> and McClure<sup>2</sup> has recently reviewed the fluorescence and effect of solvent on the fluorescence spectrum of aniline. It has been shown that the substitution at the amino group shifts the benzene fluorescence to longer wavelength side and enhances its intensity. This has been partly attributed to the contribution of the charge transfer states arising from the donor  $\text{NH}_2$  group to the benzene  $\pi$  states. Near ultraviolet emission spectrum of aniline vapour in the region of 287 to 315 nm has been reported by Kahane-Paillous<sup>3</sup>. Similarly fluorescence of benzo-trifluoride vapour has been studied by Sastri and Sponer<sup>4</sup>. The emission characteristics of aniline when substituted by a strong electron withdrawing group like the  $\text{CF}_3$  group has not been studied so far. The fluorescence spectra of isomeric trifluorotoluidines (TFT) at room temperature as well as the effect of solvent and pH on fluorescence have been studied and the results reported in this paper. The emission spectrum of TFT at low temperatures in solid glass has also been studied. The results are compared with those for aniline.

Fluorescence, phosphorescence and total emission spectra were recorded on an Aminco Bouman spectrofluorometer. Total emission at low temperature was studied in evacuated cylindrical cells without the phosphoscope attachment and the phosphorescence with the rotating cylinder phosphoscope attachment. The excitation and emission monochromator slits were 0.5 mm which were the narrowest possible. Excitation wavelength was set at the position where maximum emission is recorded.

The compounds obtained from Fluka, Switzerland, were used Spectragrade, cyclohexane, ethanol and distilled water were used to prepare the solutions after checking for solvent fluorescence. To study the effect of pH on luminescence properties, Analar  $\text{H}_2\text{SO}_4$  and NaOH solutions were added to aqueous solutions of TFT in distilled water.

The absorption spectra of isomeric TFT in solution phase show two absorption maxima, one in the range 245-250 nm and the other near 290 nm. Solution fluorescence at room temperature of the three isomers lies in the range 310 to 410 nm and wavelengths of emission maxima are given in Table 1. It is observed that the fluorescence intensity is higher for the same solution when the excitation wavelength corresponds to the longer wavelength absorption region. It is observed that the wavelengths of the fluorescence maxima are in the order  $m > o > p$  which is also the order of the longest wavelength absorption band.

It is known that solvents and pH bring about some changes in the fluorescence spectra which give some insight into the effect of substituents on the parent molecules as well as the nature of the excited state. The fluorescence spectra studied in different solvents at room temperature show that the wavelengths of the fluorescence maxima for all three isomers follow the order water > alcohol  $\approx$  cyclohexane. Solvent effect on the longest wavelength absorption, however, shows that for all the three isomers the maximum is at longest wavelength for ethanol and in water and cyclohexane, it is about the same. Thus the shift in the absorption and fluorescence maxima is largest in water. It is known that due to charge transfer contribution from the donor substituent like  $\text{NH}_2$  to the first excited singlet state, the molecule in this state has a greater dipole moment than in the ground state. This gives a larger solute solvent interaction from the excited state and as such the Franck-Condon transition from the equilibrated excited state is expected to be at considerably longer wavelengths than the corresponding absorption. Mataga

TABLE 1 — SOLUTION FLUORESCENCE AND EMISSION MAXIMA OF ISOMERIC TFT IN DIFFERENT SOLVENTS

Solvent	Absorption maximum (nm)	Excitation maximum (nm)	Fluorescence maximum (nm)	Phosphorescence maximum (nm) in EPA glass at liquid $\text{N}_2$ temp.
<i>ortho</i> -TFT				
Alcohol	241, 298	298	338	425
Cyclohexane	236, 295	296	332	
Water	235, 294	298	350	
<i>meta</i> -TFT				
Alcohol	242, 299	302	340	430
Cyclohexane	238, 295	308	336	
Water	235, 290	294	352	
<i>para</i> -TFT				
Alcohol	252, 288	291	332	412
Cyclohexane	244, 286	282	324	
Water	237, 282	290	340	

*et al.*<sup>7</sup> have discussed the solvent effect on fluorescence and the separation of absorption and fluorescence maxima on the basis of the ground and excited state dipole moment of the molecules. Their results show that shift in fluorescence as well as separation is quite larger when the excited state has pronounced increment in dipole moment. The present conclusions are quite in accordance with their findings.

The changes in fluorescence of TFT in acidic medium are similar to those observed in the case of aniline. When AnalaR H<sub>2</sub>SO<sub>4</sub> is added gradually to aqueous solution of TFT, the fluorescence intensity falls, the wavelength of maximum emission remaining the same. All the isomeric TFT show weak fluorescence even in strongly acidic solutions. In the case of aniline this weak fluorescence has been ascribed to an excited state ionization of the cation by Bridges and Williams<sup>5</sup>. At alkaline pH, the intensity of the normal fluorescence decreases and a new band near 420 nm appears. With increase in basicity, the intensity of the normal fluorescence decreases and that of the longer wavelength side emission increases. This behaviour is similar to that observed for aniline. This new band in the case of aniline has been assigned to emission due to aniline anion by Bridge and Williams<sup>5</sup>. Van Duuren<sup>6</sup> has discussed a similar effect in the case of naphthalamine.

The total emission spectra in EPA glass at liquid nitrogen temperature of all the isomeric TFT show that in addition to an emission band near 330 nm, another stronger emission band appears between 400 and 450 nm. The spectra recorded with phosphoroscope under the same condition show only the longer wavelength band. This proves that the stronger emission band between 400 and 450 nm is due to phosphorescence in all the three cases. The relative intensities of fluorescence near 330 nm and the phosphorescence near 425 nm in the total emission spectrum can be taken as proportional to quantum efficiency since both were recorded with same excitation and the detector sensitivity in this narrow range is practically uniform. It is observed that phosphorescence efficiency in *meta*- and *para*-isomers is considerably higher than fluorescence whereas in *ortho*-isomer both the properties are comparable. It may be noted that the energy separation between S<sub>1</sub> and T<sub>1</sub> which is one of the factors determining intersystem crossing is practically the same in all the three isomers as shown by spectral position. Lim and Chakraborti<sup>8</sup> have shown that intramolecular charge transfer transitions make significant contribution to the spin-orbit coupling and are important sources of intensity for the phosphorescence of such molecules. They have further remarked that the enhanced phosphorescence to fluorescence quantum yield ratios of aromatic anions are due to such increased spin orbit coupling. Present results, hence, show that CF<sub>3</sub> group enhances the contribution of charge transfer character compared to aniline on *meta*- and *para*-isomers more than in *ortho*-isomer.

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### Crystal Data & Thermal Behaviour of Morpholinium Aluminium Sulphate [(morphH)<sub>2</sub>SO<sub>4</sub>·Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·24H<sub>2</sub>O]

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The interaction of morpholinium sulphate and aluminium sulphate results in the formation of morpholinium sulphate aluminium sulphate [(morphH)<sub>2</sub>SO<sub>4</sub>·Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·24H<sub>2</sub>O]. The X-ray powder diffraction pattern indicates that the crystal belongs to cubic system with a cell constant of 12.24 Å. The thermal behaviour of the compound has also been studied.

AS a part of our general study on the formation and properties of double salts featuring morpholinium and metal ions, the preparation and characterization, by X-ray and thermal studies, of morpholinium aluminium sulphate, [(morphH)<sub>2</sub>SO<sub>4</sub>·Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·24H<sub>2</sub>O] are reported in this note.

To a hot aqueous solution containing 13.3 g Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·18H<sub>2</sub>O in 60 ml water was added 5.4 g (morphH)<sub>2</sub>SO<sub>4</sub> in 15 ml water and a few drops of 2N H<sub>2</sub>SO<sub>4</sub>. The contents were stirred for 15 min, the clear solution kept aside, the separated colourless crystals filtered, washed with acetone and dried; m.p. 94° (Found: C, 9.21; H, 6.48; N, 2.72; S, 12.28; Al, 5.32. C<sub>8</sub>H<sub>68</sub>N<sub>2</sub>S<sub>4</sub>O<sub>42</sub>Al<sub>2</sub> requires C, 9.18; H, 6.55; N, 2.67; S, 12.26; Al, 5.15%).

The X-ray powder diffraction pattern was taken on a Philips PW 1041 X-ray diffractometer using CuK<sub>α</sub> radiation. The thermogravimetric analysis was made in air using Stanton recording thermobalance at a linear heating rate of 6° min<sup>-1</sup> in mullite crucible container. The differential thermal analysis was carried out on a Netzsch differential thermal analyser using inert alumina as reference material. The heating rate of the furnace was kept at 10° min<sup>-1</sup>.

The X-ray diffraction pattern is indexed<sup>2</sup> for the cubic system and the unit cell dimension is calculated to be 12.24 Å. The density of the crystals measured pycnometrically is found to be 1.868 g cm<sup>-3</sup> while that calculated for 4 formula units of (morphH)Al(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O, from the unit cell constant is 1.895 g cm<sup>-3</sup>. The X-ray data suggest that the double salt is isomorphous with the alum<sup>1</sup> whose unit cell lengths vary from 12.13 to 12.70 Å.

Depending on the packing, the alums are classified into α-, β- and γ-forms<sup>3</sup>. A bulky [H<sub>3</sub>CNH<sub>3</sub>]<sup>+</sup> cation forms two types of methylammonium alums,