

RESEARCH NOTE

OPTICAL SPECTRA OF 2-AROYL-5-AROYLAMINO DERIVATIVES OF 2H-1,2,4-THIADIAZOLINE-3-ONE

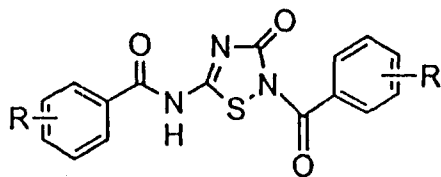
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Abstract — Optical spectra of 5-amino-2H-1,2,4-thiadiazoline-3-one (AT) and some 2-aryl-5-arylamino derivatives are reported. Absorption spectra of 2-aryl-5-arylamino derivatives show bathochromic shift due to AT group and other substituents of phenyl ring. Weak emission is observed for some derivatives.

INTRODUCTION

Aroyl derivatives of 5-amino-2H-1,2,4-thiadiazoline-3-one (AT) which is a 5-membered ring analog of cytosine, are interesting in many aspects. While heterocyclic compounds like 1,2,4-thiadiazole are aromatic,¹ the aromaticity related with tautomerism of AT is in question. The ¹³C NMR spectra of AT suggests that AT has as the lactam form.² Amino and aroyl groups show auxochromic shift and the ring substituents of aroyl group are important in the study of molecular structure effect on the electronic spectra. Nonbonding lone-pair electrons which are rich in the derivatives of AT, form a new bond in acidic solution to modify the electronic spectra.³



As acyl derivatives of cytosine show bioactivities,⁴ aroyl derivatives of AT are expected to be bioactive.

MATERIALS AND METHODS

AT is synthesized from reaction of 2-thiobiuret in hydrogen peroxide-basic solution⁵ and 2-aryl-5-arylamino derivatives of AT are obtained by acylation with aroyl chlorides.⁶ Methoxy, nitro or chloro group is substituted in phenyl ring of aroyl group. Recently synthesis of

similar derivatives have been reported.⁷ No good solvents for optical spectra of aroyl derivatives of AT are available. These compounds are only slightly soluble in hot water and soluble in dimethylformamide which has strong absorption in the UV region. Absorption and emission spectra are taken in aqueous solution at room temperature. As only small amount of the compounds are soluble in water, it was difficult to determine extinction coefficients quantitatively. It is roughly estimated that the extinction coefficients for the peak maxima are in the range of 10^2 and 10^3 . A quartz cell of 1 cm optical length is used for the spectrum record. Absorption and emission spectra are taken with CARY3 uv/visible spectrophotometer and SLM-Aminco 4800 spectrofluorometer, respectively.

RESULTS AND DISCUSSION

Aroyl derivatives of AT have two chromophore groups - 5-membered ring of AT and aroyl groups. The 5-membered ring of AT consists of two conjugated double bonds and the aroyl group is considered to show similar spectra as benzamide derivatives. Amino group induces bathochromic shift in 1,2,4-thiadiazole.⁸ While a spectral maximum is observed at 229 nm for 1,2,4-thiadiazole, the maximum appears at 247 nm for 5-amino derivative and at 256 nm for 2,5-diamino derivative.

Figure 1 shows spectra of AT and 2-benzoyl-5-benzoylamino-1,2,4-thiadiazoline-3-one (BBAT). The spectrum of AT shows a maximum at 245 nm as like 5-amino-1,2,4-thiadiazole and no absorption at the longer wavelength. The absorption peak of BBAT in the longer wavelength region is attributed to aroyl groups. The spectrum of BBAT is considered as a sum of AT and benzamide spectra. The spectrum of benzamide shows an intense peak at 225 nm due to carbonyl group and small absorbance around 268 nm from π - π^* transition of phenyl ring.⁹ The n - π^* transition of carbonyl groups show absorp-

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tion maximum at the wavelength shorter than 220 nm for aliphatic amides. For bezamide, the absorption of carbonyl group shifts to longer wavelength by electron donating phenyl group. For BBAT, the absorption of phenyl group of BBAT shifts to around 275 nm and the intensity is greater than benzamide because of a strong bathochromic effect of AT group.

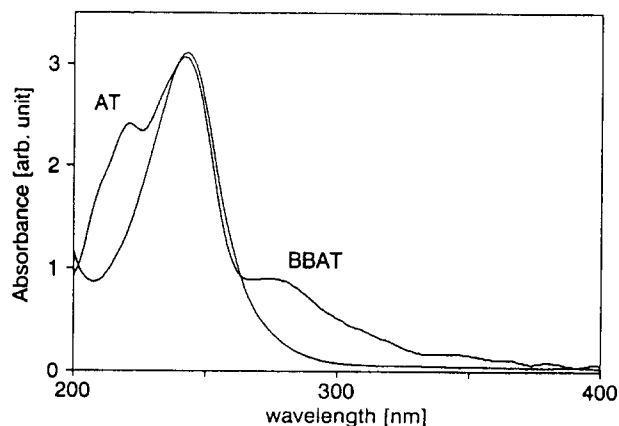


Figure 1. Absorption spectra of 5-amino-2H-1,2,4-thiadiazoline-3-one(AT) and 2-benzoyl-5-benzoylamino-1,2,4-thiadiazoline-3-one (BBAT).

If AT is aromatic, the length of conjugated orbitals increases in BBAT so that the absorption peak at 245 nm will shift to the longer wavelength. No change of the peak indicates that AT is not aromatic and it is consistent with the lactam form of AT.

Absorption spectra of anisoyl and chlorobenzoyl derivatives of AT are shown in Figure 2. Larger bathochromic shift of the phenyl ring absorption, which is considered as the effect of the ring substituent groups, is observed for these derivatives. Spectra

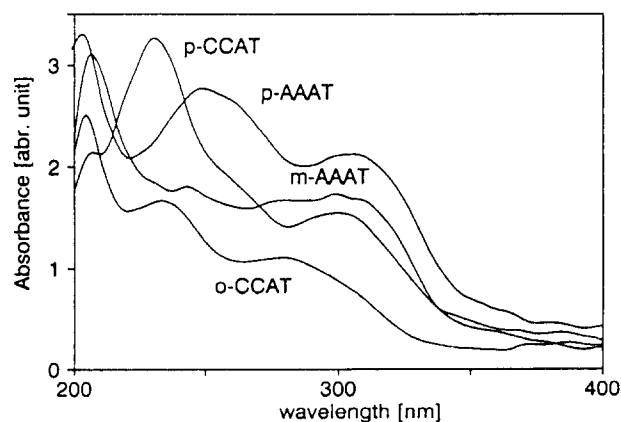


Figure 2. Absorption spectra of 2-anisoyl-5-anisoylamino-1,2,4-thiadiazoline-3-one (AAAT) derivatives and 2-chlorobenzoyl-5-chlorobenzoylamino-1,2,4-thiadiazoline-3-one (CCAT) derivatives. The prefix indicates the position of substituent in aroyl group.

of anisoyl derivatives are consistent with spectra of anisamides,⁹ and it also confirms that AT is lactam form. Larger shift for *para*-substituent is well-known.¹⁰

Absorption spectra of three nitrobenzoyl derivatives are shown in Figure 3. Spectra different from above other derivatives are attributed to charge transfer from phenyl ring to nitro group. Aromatic nitro compounds are known to show complicated photochromism.¹¹

Although fluorescence spectra also show auxochromic shift¹¹, no significant effects are found in the emission spectra for the aroyl derivatives of

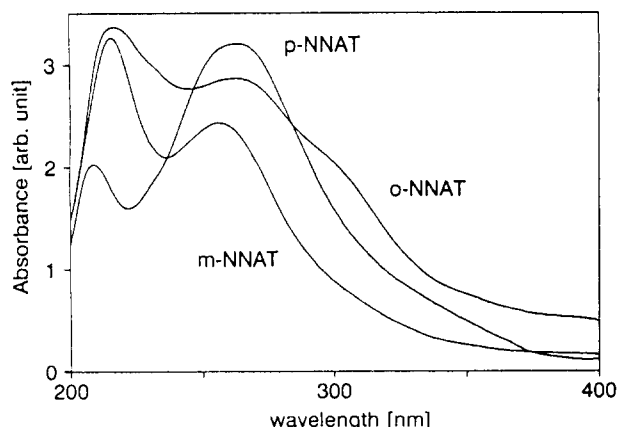


Figure 3. Absorption spectra of 2-nitrobenzoyl-5-nitrobenzoylamino-1,2,4-thiadiazoline-3-one (NNAT) derivatives. The prefix indicates the position of substituent in aroyl group.

AT. Most compounds show weak and broad emission spectra and emission from AT, p-NNAT and p-CCAT was negligible. Typical emission spectrum of an aroyl derivative is shown Figure 4. Similar shift of the emission maximum from the excitation wavelength is observed for other derivatives.

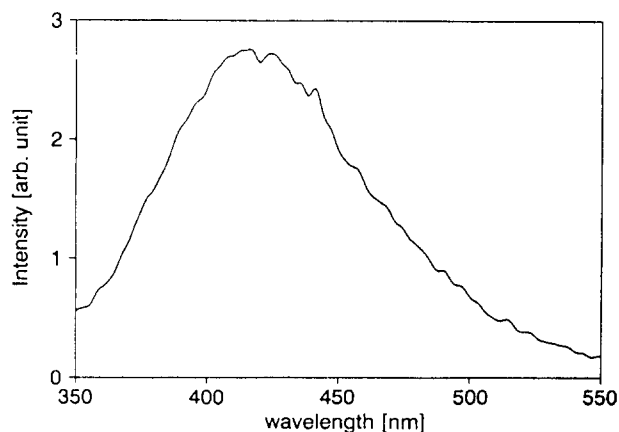


Figure 4. Emission spectra of 2-(m-anisoyl)-5-(m-anisoylamino)-1,2,4-thiadiazoline-3-one. Excitation wavelength is 320 nm.

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