

Characteristics of Some Derivatives of Tetraazaindene

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Abstract

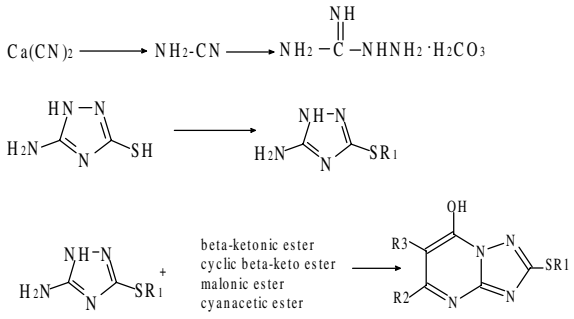
Some derivatives of tetraazaindene were synthesized. The method of their synthesis were given. UV, IR, NMR, and mass Spectra were studied to characterize their chemical structure. Photographic behaviors related to chloride-rich emulsion of these compounds were determined by adding the compound into chemical sensitized emulsion and chemical as well as spectral sensitized emulsion respectively. Ka and K_{sp} values of the compounds were measured, and adsorption properties of the compounds to AgCl crystal from their solutions were studied.

Introduction

Since E. J. Birr[1] found, that 4-hydroxy-6-methyl-1,3,3a,7-tetraazaundene (TAI) was an effective stabilizer for silver halide emulsion in 1935, numerous papers and patents were published about the stabilizers and antifoggants. Recently, T. Tani[2] reviewed the stabilizers, particularly concentrated on the mechanism of stabilizers of photographic emulsions. In this paper, some derivatives of tetraazaindene, their synthesis and characteristics, are reported.

Experimental

Derivatives of TAI were synthesized by the route as:



Structure of synthesized compounds and TAI all shown as Tab. 1:

Tab. 1. Structure of synthesized compounds and TAI

Compound No.	R1	R2	R3
1(TAI)	-	Me	H
2	Me	Me	H
3	Me	Me	Et
4	Me	Me	n-Pr
5	Me	Me	n-Bu
6	Me	Me	$HOCH_2CH_2$
7	Et	Me	H
8	Me	OH	H

Dissociation constants (pKa's) were measured by titration with KOH solution under the control of a pH water. They were calculated by the Eq. 1:

$$pKa = pH - \log\frac{cv}{c_0v_0 - cv} \qquad \text{(Eq.1)}$$

where c_0 - concentration of stabilizer;

v_0 - volume of stabilizer solution;

c - concentration;

v - volume of KOH solution.

Solubility constants (pK_{sp}'s) of Ag salts of of stabilizers were determined by the isoelectric points, which were obtained by potential titration with solution of sodium tetraborate.

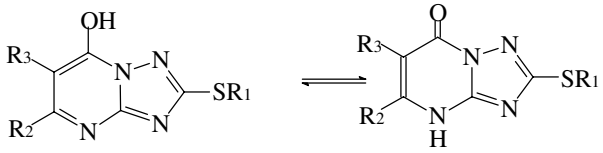
Photographic behaviors were determined by adding the stabilizer into a rich-chloride photographic emulsion. A chemical sensitized emulsion with monodispersed cubic silver halide grains (Cl: Br=99.5: 0.5; crystal size=0.75μm) was used. After stabilizer was added, the coated emulsions were kept under 65ºC and 80% RH determine their photographic behaviors.

Results and Discussion

1. Characteristics of structure of the compounds

Structure of synthesized of the compounds were characterized by UV-VIS, FT-IR and HNMR spectra.

The absorption peaks in IR spectra of some of compounds are listed in Tab. 2. It is found, that most of the compounds (except compound No.8) have both of vibrational absorption of NH group and C=O group. Thus, these compounds exist in tautomic form:

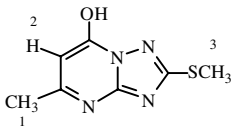
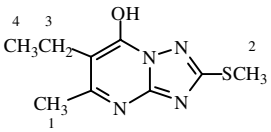
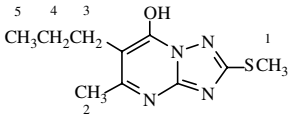
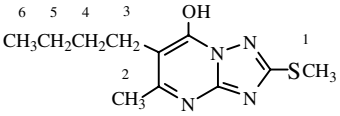
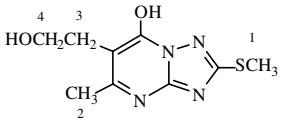
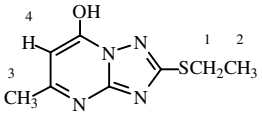
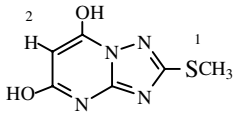


Tab. 2. Absorption peaks in IR spectra of some derivatives of TAI

Compound No.	υ_{OH} cm^{-1}	υ_{NH} cm^{-1}	υ_{CH} cm^{-1}	υ_{SR} cm^{-1}	υ_{CO} cm^{-1}
2	3308	3212	2957	2831	1694
3	3323	3232	2966	2827	1694
4	3145	3071	2957	2857	1652
5	3245	3049	2980	2765	1683
6	3241	3049	2980	2865	1682
7	3142	3207	2982	2864	1659
8	3468		2964	2851	

Characteristics of HNMR spectra of above-mentioned compounds all listed in Tab. 3. These characteristics confirm the structure of these compounds.

Tab. 3. Characteristics of HNMR spectra of some derivatives of TAI

Compound No.	Structure	Data of HNMR
2		1: 2.25（s, 3H） 2: 5.80（s, 1H） 3: 2.47（s, 3H）
3		1: 1.82（s, 3H） 2: 2.47（s, 3H） 3: 2.28（s, 2H, J=7.6） 4: 1.03（t, 3H, J=7.6）
4		1: 2.47（s, 3H） 2: 2.05（s, 3H） 3: 2.35（m,2H, J=7.2） 4: 1.41（m,2H, J=7.0） 5: 1.08（t, 3H, J=7.1）
5		1: 2.48（s, 3H） 2: 2.04（s, 3H） 3: 2.38（t, 3H, J=7.0） 4: 1.28（m,2H, J=7.1） 5: 1.34（m,2H, J=7.1） 6: 0.85（t, 3H, J=7.0）
6		1: 2.50（s, 3H） 2: 2.09（s, 3H） 3: 2.58（t, 2H, J=6.9） 4: 3.52（t, 2H, J=6.8）
7		1: 2.65（m,2H, J=7.3） 2: 1.13（t, 3H, J=7.2） 3: 2.24（s, 3H） 4: 5.79（s, 1H）
8		1: 2.45（s, 3H） 2: 5.13（s, 1H）

2. Photographic behaviors

The stabilizing effect of the compounds is listed in Tab. 4. (with No. 9 for a comparison)

Tab. 4 Stabilizing effect of some derivatives of TAI

Compound No.	D_{min} with aging time (day)			
	0	1	2	3
1	0.16	0.23	0.41	1.75
2	0.14	0.20	0.42	1.65
3	0.17	0.36	0.68	2.39
4	0.26	0.45	1.14	2.41
5	0.32	0.52	1.26	2.40
6	0.19	0.28	0.66	1.73
7	0.22	0.31	0.56	1.40
8	0.33	0.64	1.56	2.49
9†	0.22	0.35	0.61	1.01

† 3-phenyl-5-mercapto-tetrazole

Similar to TAI, those compounds also have some sensitizing effect. (Tab. 5)

Tab. 5 Sensitizing effect of some derivatives of TAI

Compoumd No.	Amount added in emulsion mmol/molAg	Relative sensitivity
Blank	0	100
1	3	124
2	3	120
3	3	113
4	3	116
5	3	106
6	3	130
7	3	109
8	3	70
9	0.6	105

From Tab. 4 and 5, it can be found, most of the compounds have the similar photographic behaviors to TAI, only compound No. 8 has not as much sensitizing effect as other compounds.

3. Ka and K_{sp} values

Five synthesized compounds have been used to measure their Ka's. The results are shown is Tab. 6.

Tab. 6 Dissociation contants of some derivatives of TAI (25℃)

Compound No.	pKa	Remark (data from ref.)
1	6.29	6.27[3], 6.34[4], 6.35[5]
2	6.61	6.23[3], 6.21[5]
3	7.56	
4	7.26	
5	7.73	
7	6.86	

It can be found from Tab. 6, that comparing with compound No.1 alkylthio-group in 2-position of the compound increases pKa value, while alkyl-substituent in 5-position increases pKa to a much greater extent.

pK_{sp}'s obtained in this experimental work, are shown in Tab. 7.

Tab. 7 Solubility products of some derivatives of TAI

Compound No.	pK_{sp}	Remark (Data from Ref.)
1	10.4	9.7[1], 10.1[5], 10.15[4], 10.5[2], 10.52[6]
2	10.1	9.9[5], 9.94[4],
3	——	no ppt.
4	11.0	——
5	10.9	——
6	——	non-reproducible
7	——	no ppt.
8	11.4	——

Most of the compounds have the pK_{sp}'s similar to compound No.1. However, a reproducible value could not been found with compound No.6, since these was a hydroxy group in its 5-position, this hydroxy group might also coordinate with silver ion and confuse the result.

Conclusion

Derivatives of TAI were Synthesized. Their pK_{sp}'s, pKa's and photographic behaviors have been determined. Their characteristics are similar to those of TAI. Their antifogging abilities are lower than those of 3-phenyl-5-mercapto-tetrazole, and their pK_{sp}'s are also lower than those of 3-phenyl-5-mercapto-tetrazole.

References

1. E. J. Birr, "Stabilization of Photographic Silver Halide

Emulsions", New York: Focal, (1974)

2. Tadaaki Tani, Photography Sensitivity, Chapter 8, New York: Oxford , (1995)
3. Tadaaki Tani, Sensitization by Hydroxy-tetraazaindenes, Photogr. Sci. Eng., 21(1): 37-47 (1977)
4. J. Pouradier, A. Pailiotet, F. Garatin, Siver Sailts of 4-Hydroxy-6-methyl-1,3,3a,7-tetraazaindene and of Its 2-methylmercapto Derivative, J. Photogr. Sci., 29: 83-86 (1981)
5. Roger L. Klaus, Fundamental Solution Properties of 4-Hydroxy-1,3,3a,7-tetraazaindenes, J. Imag. Sci. Tech., 42(6): 523-527 (1998)
6. G. P. Faerman, Investigation on the Effect of Organic Anti-foggants on the Development Process, J. Photogr. Sci., 15: 22-28 (1967)

Biography*

- 1953, Graduated from East China Institute of Chemical Technology, Shanghai, China;
- 1956, Completed graduate study in Dalian Institute of Technology , Dalian, China;

1956 - 1980, Lecture, East China Institute of Chemical Technology, Shanghai, China;

1980 - 1982, Visiting Scholar, Northwestern University, USA;

1982 - 1994, Professor, East China University of Science and Technology, Shanghai, China;

1994 - present, professor, Shanghai Jiao Tong University, Shanghai, China.