different from that of the solution to be titrated, or a mixed solvent is used. Glass electrode was found to function properly and stable in acidic solvents, and high accuracy and precision can be expected by this method.

If the solvent of titrant is *p*-dioxane instead of acetic acid, it can be determined more sensitively, especially when the basicity of the sample is rather stronger in the solvent (cf. Figs. 2, 3, and 5).

Estimating by the half-neutralization point of the potentiometric titration curve,[3] the effect on titration of the combined nitric acid residue of the diphenhydramine salt is larger than that of phosphoric acid, but by the differential titration curve the effect of the former is smaller than that of the latter. It would be caused by the effect of the second dissociation of phosphoric acid near the end point, so the end point of salt of organic base could not determine very accurately by ordinary method.

The author is indebted to Dr. T. Kariyone, Director of the Laboratory, Dr. K. Nagasawa and Dr. Y. Nozaki for their kind encouragements and advices, and wishes to thank Messrs. M. Tsuchiya and K. Kano for their valuable assistance in the preparation of the reagents.

Summary

Direct differential potentiometric titrations in nonaqueous solutions were carried out using two glass electrodes, one of which is used as a retarded electrode. One and the greatest disadvantages of nonaqueous potentiometric titrations employing a reference electrode whose solvent is different from that of the solution or of the titrant, the fluctuation of liquid junction potentials between the two solutions of different solvents, can be overcome by this method.

This method applied to the determinations of four derivatives of 1-phenyl-3-methyl-3-pyrazolin-5-one and several acid salts of diphenhydramine in anhydrous acetic acid solution with perchloric acid in acetic acid or *p*-dioxane as the titrant, was shown to give satisfactory and reproducible results.

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40. **Tsukasa Kuraishi**: 4,5-Substituted Pyridazines. IV.[1] The Effect of Some Substituents at the 4-Position on the Ultraviolet Absorption Spectrum of 3,6-Dichloropyridazine.

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Recently, studies of the near-ultraviolet absorption spectra of diazines have been extended by several workers. Particulary, much attentions have been paid to the weak absorption band arising from a non-bonding nitrogen electron transition.[2] In preliminary works the present writer studied the vibrational spectra of the diazines and electronic spectra of the weak absorption of pyrazine vapor.[3] In order to investigate the effect of some substituents at the 4-position of pyridazine ring on the ultraviolet absorption spectra, the absorption maxima of several compounds of the following type

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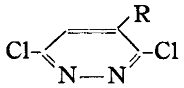
* Showa-machi, Nagasaki (倉石 典).

1) Part Ⅲ: This Bulletin, **5**, 587(1957).

2) For discussion of $n-\pi^*$ and $\pi-\pi^*$ transition of the diazines, see F. Halverson, R.C. Hirt: J. Chem. Phys., **19**, 711(1951); R.C. Hirt, F.T. King, J.C. Cavagnol: *Ibid.* **25**, 574(1956); R.H. Hornig, E.D. Amstutz: J. Org. Chem., **20**, 1069(1955).

3) M. Ito, R. Shimada, T. Kuraishi, W. Mizushima: J. Chem. Phys., **25**, 574(1956); **26**, 1508(1957).

were examined.



R=H, CH_3, Cl, OC_2H_5, NH_2, $NHNH_2$

In 1951, Halverson and Hirt[2] studied the solution spectra of pyridazine, 3,6-dichloropyridazine, etc. Absorption spectra of a number of pyridazine derivatives were reported by Druey, *et al.*[4] in 1954, although they did not give its assignment in detail. In this paper, the writer presents the experimental results of solution spectra for the argument that these bands consist of four absorption series which belong to different electronic transitions.

Experimental and Results

The samples used in this study were prepared by the method described in previous papers[5] and purified by repeated recrystallization.

The ultraviolet absorption spectra in the near-ultraviolet region were measured with a Beckman Model DU spectrophotometer using EtOH (99%) and cyclohexane as a solvent. Band positions are given in mμ and in wave numbers (Kaysers), and intensities as molar absorptivities (ε). The absorption maxima are summarized in Table I.

Table I. Absorption Maxima of 4-Substituted 3,6-Dichloropyridazines (in mμ)

	R=H	R=CH_3	R=Cl	R=OC_2H_5	R=NH_2	R=$NHNH_2$	solvent
1st	306	298	306	—			EtOH
band	324	315	321	shoulder			cyclohexane
2nd	270	270	278	270	295	290	EtOH
band	276	276	280	271			cyclohexane
3rd	—	—	shoulder	230	257	261	EtOH
band	—	—	223	235			cyclohexane
4th	216	217	213	212	219	213	EtOH
band	—	—	—	—			cyclohexane

Discussion

In the vapor spectra of diazines, two absorption band systems are observed. One near 30000 K (referred to as the first band) is considered to be due to the transition of non-bonding electrons which would occupy one of the sp^2 orbitals, and another observed near 40000 K (referred to as the second band) of a strong intensity has been known as the transition between π-electron systems. Halverson and Hirt assigned A_1-A_1(36800 K) and A_1-B_1(32900 K) transitions for the band of 3,6-dichloropyridazine and other diazine

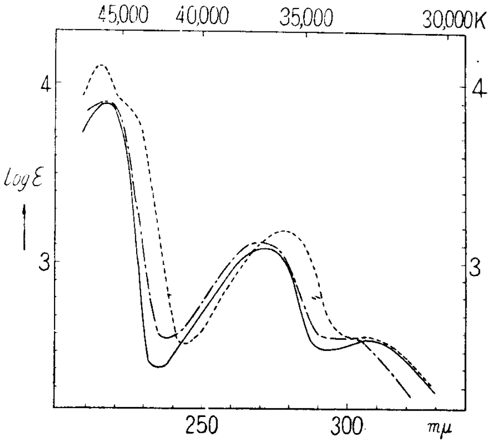
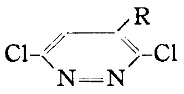


Fig. 1.

Ultraviolet Absorption Spectra (in EtOH)



—— R=H

------ R=Cl

— — R=CH_3

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4) K. Eichenberger, J. Druey, R. Rometsh : Helv. Chim. Acta, **37**, 1298(1954).

5) T. Kuraishi : This Bulletin, **4**, 137(1956); **5**, 376(1957).

compounds from valence bond calculation.

Although solvent effect was not examined in detail in this study, a similar assignment will be possible for the absorption spectra of 4-methyl-3,6-dichloro- (298 and 270 mμ) and 3,4,6-trichloropyridazine (306 and 278 mμ). 4-Ethoxy, 4-hydrazino and 4-amino compounds did not show the first band. This band probably shifts toward shorter wave lengths and may be covered by the strong second band.

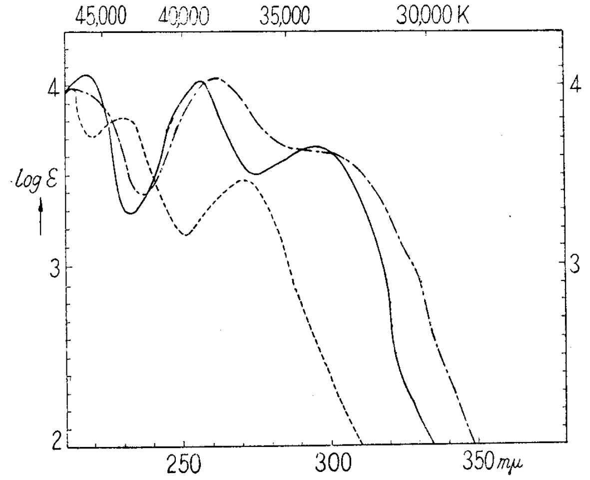
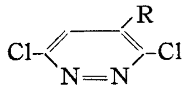


Fig. 2. Ultraviolet Absorption Spectra



—— $R=NH_2$

------ $R=OC_2H_5$

— — $R=NHNH_2$

in EtOH

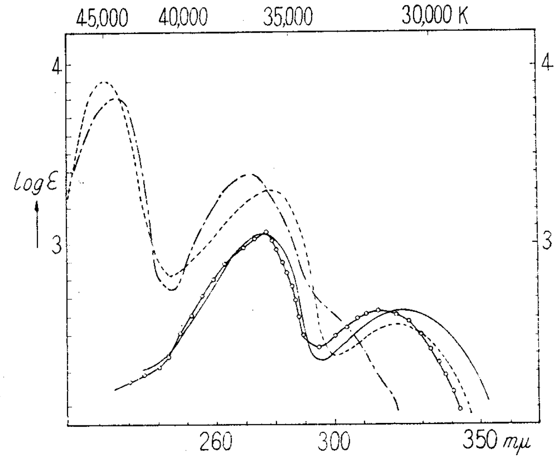
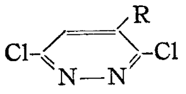


Fig. 3. Ultraviolet Absorption Spectra



—— $R=H$

-o—o- $R=CH_3$

-------- $R=Cl$

— — — $R=OC_2H_5$

in cyclohexane

Actually, the absorption maxima of the first band for some compounds in cyclohexane solution shifted toward the longer wave length. This hypsochromic shift of the first band in ethanol solution is considered to be due to the fact that in proton-donor solvents such as ethanol and water the non-bonding orbital is stabilized as a result of hydrogen-bond formation. Further indication of hydrogen bonding is observed in the second band ($\pi-\pi^*$), where the solvent effect of the band appears as a strong hypsochromic shift in going from cyclohexane to ethanol.

At any rate, it has been observed that the character of the first band shifts toward a shorter wave length by the substitution of hydrogen atom at the 4-position with such a group.

On the other hand, the higher energy band (2nd band) shifts conversely toward a longer wave length. This phenomenon is in accordance with the spectra of benzene and its monosubstituted derivatives.[6)]

In general, the electronic transition of absorption band (A_{1g}-B_{2u}) in benzene shifts toward a longer wave length as the ionization potential of the substituent decreases. Therefore, it will be expected in this case also that the order of shift of the second band toward a lower energy is inversely proportional to the ionization potential of the substituent, and in the reverse direction for the first band. However, the second band of the 4-ethoxy compound appeared in a shorter wave length than that of 3,6-dichloropyridazine in cyclohexane solution.

The third band of strong intensity appears respectively at 230, 261, and 257 mμ, and as a shoulder for the 4-ethoxy, 4-hydrazino, 4-amino, and 3,4,6-trichloro compounds in ethanol solution. It is difficult to correspond these absorption bands to the bands of

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6) W. W. Robertson, F. A. Matsen: J. Am. Chem. Soc., **72**, 5244(1950).

3,6-dichloropyridazine because it is unusual to expect these large shift of the wave length as are observed in the cases of 4-ethoxy, 4-hydrazino, and 4-amino compounds. In order to explain the experimental results, it is considered that the third band may be due to a transition which occurs from interaction between the lowest vacant level of pyridazine ring and the highest occupied level of the substituent; accordingly, it would be similar in nature to the band of nitrobenzene located at 260 mμ and of benzoic acid at 230 mμ. The reason for the appearance of this band in 3,4,6-trichloropyridazine as a shoulder in a rather shorter wave length in ethanol solution is considered to be similar to the case of chlorobenzene.[7]

Finally, the fourth band which has absorption maximum at about 210 mμ for all these compounds is regarded as the $\pi-\pi^{**}$ transition, where π^{**} is a π level lying above the π^{*} level relative to the first and second bands. In cyclohexane solution, as shown in Fig. 3, this band seems to have shifted to a shorter wave length side.

Thus, in spite of its simplicity, the present qualitative explanation may be able to explain the experimental results obtained up to the present.

The writer expresses sincere thanks to Prof. M. Yanai for his encouragement throughout this work, and to Mr. A. Matsuura for his assistance in carrying out a part of experiments. The writer is indebted to the Ministry of Education for the Grant in Aid for Scientific Research for this work.

Summary

Ultraviolet absorption spectra of some 4-substituted 3,6-dichloropyridazines were measured and qualitative explanation of the bands was presented. Solvent effect and substituent effect at the 4-position of pyridazine ring were compared with those of 3,6-dichloropyridazine.

(Received November 16, 1957)

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[7] S. Nagakura, J. Tanaka: Nippon Kagaku Zasshi, **75**, 331(1954).