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Chemical Species Produced from Some Diazaazulene Derivatives in Aqueous Solutions of Various Acidities

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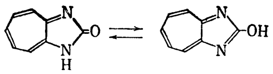
Making use of the isosbestic points which appear in equilibrium between two chemical species, the chemical structures of various species produced from the diazaazulene derivatives have been investigated in aqueous solutions over a wide pH range. For 1-hydro-1,3-diazaazulene-2-one (abbreviation, HDA-1), for instance, four different species exist as stable species in the respective regions; (a) the pH region higher than 12, (b) around the neutral state, (c) the pH value of *ca.* 1.5, and (d) the strong acid state. In the (a) region, H^+ is taken off from the amino nitrogen of HDA-1 and the species becomes HDA-1^-; in (b) the species takes the HDA-1 structure, as its name indicates; in (c) it takes the H^+-HDA-1 structure protonated at the aza nitrogen, and in (d) it takes the H^+-HDA-1-H^+ structure, in which the position of the second protonation could not be clarified. In the case of 2-ethoxy-1,3-diazaazulene (EDA-2), the species corresponding to the second protonation (H^+-EDA-2-H^+) is hydrolyzed by acid catalysis and becomes H^+-HDA-1-H^+. In order to interpret the spectra of azaazulene compounds and the spectral change due to protonation, calculations by the LCAO–ASMO–SCF–CI method have been made for 1,3-diazaazulene and EDA-2. The characters of the first and the second transitions of the compounds have been satisfactorily explained by the diagrams of the AO coefficients of the LCAO-MO's representative of the transitions.

In the past two decades, a number of azaazulene compounds have been synthesized as tropolone derivatives. However, only a few physico-chemical studies have been reported, such as one on the dipole moment by Kurita and Kubo[1], and one on the electronic spectra by Nozoe and Murata.[2] As for the theoretical treatment, there seems to have been nothing except the study by Kon[3] using the simple molecular orbital method.

Nozoe *et al.*[4] have considered the product of the reaction of tropolone-methylether and guanidine hydrochloride to be a mixture of 2-amino-1,3-diazaazulene and 1-hydro-2-imino-1,3-diazaazulene, which are tautomer with each other. Similarly, it is considered that a tautomerism exists between 2-hydroxy-1,3-diazaazulene (to be henceforth abbreviated as HDA-2) and 1-hydro-1,3-diazaazulene-2-one (HDA-1) as follows;



HDA-1 HDA-2 (1)

where the mole ratio of HDA-1 and HDA-2 in the methanolic solution is considered to be about 7:3.[5,6] If such an equilibrium as Eq. (1) exists, some spectral change may be expected to occur for the system when the temperature is changed. In order to determine the temperature dependence of the spectra, we measured the absorption spectra in ethanolic and aqueous solutions over the range from 25°C to 55°C. An appreciable change in spectra appeared, but the magnitude and the behavior of the spectral change were almost the same as those in the case of azulene in an ethanolic solution, in which no tautomerism like that of Eq. (1) is involved. For this reason, it is very doubtful that the above-mentioned system contains two chemical species as Eq. (1) indicates.

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1) Y. Kurita and M. Kubo, *J. Amer. Chem. Soc.*, **79**, 5460 (1957).

2) T. Nozoe and T. Murata, *Proc. Japan Acad.*, **30**, 482 (1954).

3) H. Kon, *Sci. Repts. Tohoku Univ. I*, **38**, 67 (1954).

4) T. Nozoe, T. Mukai, K. Takase, I. Murata and K. Matsumoto, *Proc. Japan Acad.*, **29**, 452 (1953).

5) T. Nozoe, T. Mukai and I. Murata, *J. Amer. Chem. Soc.*, **76**, 3352 (1954).

6) I. Murata, *Sci. Rep. Res. Inst., Tohoku Univ., Ser. A*, **12**, 271 (1963).

A tautomerism is also considered to exist between anthrone and anthranole; the ratio is said to be dependent on the amount of the alkaline substance (triethylamine) added to the system.[7] If this is true, the equilibrium between HDA-1 and HDA-2 of Eq. (1) should also be shifted by the variation in the nature of the solvent, for example, by the variation in the pH of the solution. In fact, the aqueous solutions of HDA-1 show a considerable change in spectra, while retaining definite isosbestic points, upon pH variation.

In the present investigation, the chemical structures of species produced from the azaazulene derivatives in the various pH regions will be clarified.

Azulene is well known as an isomer of naphthalene; it has been investigated in detail both theoretically[8] and experimentally.[9] Concerning the diazaazulene derivatives, however, there has been only one theoretical treatment, one by Kon[3] carried out by the Hückel method. Therefore, the electronic spectra of 1,3-diazaazulene and 2-ethoxy-1,3-diazaazulene will be calculated, and the results will be discussed with reference to those for azulene, which has previously been computed using the same approximation.[10]

Experimental

The 2-ethoxy-1,3-diazaazulene and 1-hydro-1,3-diazaazulene-2-one were provided by the Sankyo Company, Ltd. The 1-ethyl-1,3-diazaazulene-2-one was synthesized following Reference 11. The melting points were determined to be 101—102°C (lit, 101°C),[11] 243°C (245°C),[4] and 138°C (140°C)[12] respectively.

The concentrations of the samples used were of the order of 10^{-4} mol/*l*. The pH value of the solution was controlled by hydrochloric acid and sodium hydroxide, and was measured by means of a Toa Denpa pH meter, HM 5A. A strong acid or a strong alkaline solution of the sample was prepared by using concentrated sulfuric acid or sodium hydroxide respectively. The conditions of the solutions used are illustrated in the figures.

The measurement of the absorption spectra was carried out by a Shimadzu MPS-50A Recording Spectrophotometer over 220—400 mμ.

Results

Figure 1 shows the absorption spectra of 1-hydro-1,3-diazaazulene-2-one (abbreviation, HDA-1) in alkaline solutions with various pH values. The isosbestic points indicate the presence of two kinds of species in equilibrium. No further spectral change appeared upon an increase in the alkaline strength to more than pH=12.4 (by 0.5N of NaOH).

Figure 2 shows the absorption spectra of HDA-1 in the week acid region of pH=5.9—1.5. In this case, isosbestic points also appear, indicating an

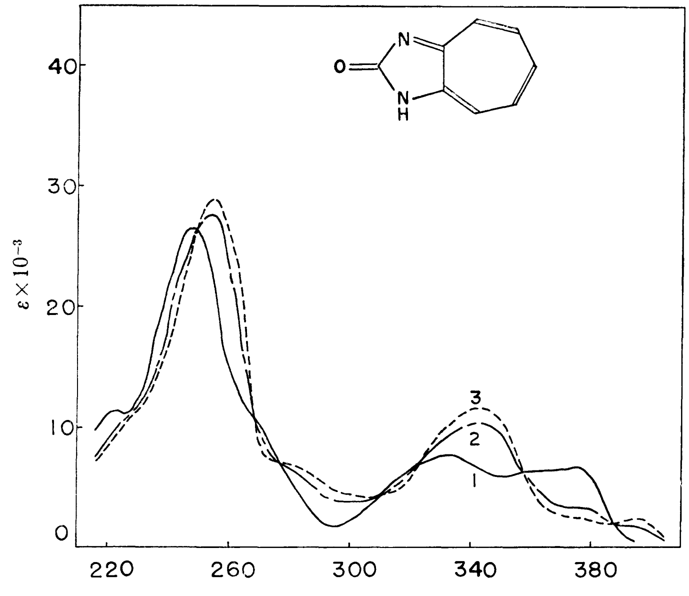

Fig. 1. Absorption spectra of (HDA-1) in aqueous alkaline solutions.
1. pH=6.10, 2. pH=10.0, 3. pH=12.40

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[7] H. Baba and T. Takemura, This Bulletin, **37**, 1241 (1964).

[8] R. Parizer, *J. Chem. Phys.*, **25**, 1112 (1956); E. Heilbronner, "Non-Benzenoid Aromatic Compounds," D. Ginsburg, ed., Interscience, N. Y. (1960), p. 171.

[9] J. W. Sidman and D. S. McClure, *J. Chem. Phys.*, **24**, 757 (1956); G. R. Hunt and I. G. Ross, *J. Mol. Spectry.*, **3**, 604 (1959); **9**, 50 (1962).

[10] Y. Tanizaki, T. Kobayashi and T. Hoshi, to be published.

[11] G. Sunagawa and M. Watatani, *Chem. Pharm. Bull.* (Tokyo), **16**, 1308 (1968).

[12] H. Nakao, N. Soma, Y. Sato and G. Sunagawa, *ibid.*, **13**, 473 (1965).

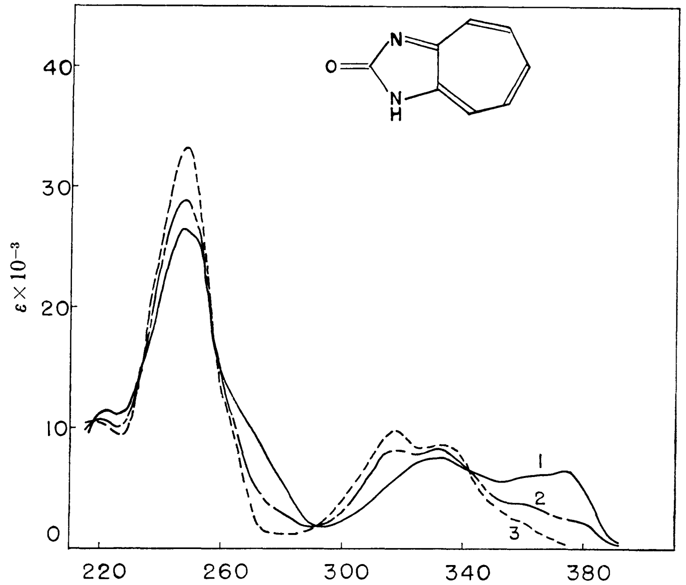

Fig. 2. Absorption spectra of (HDA-1) in aqueous acid solutions.
1. pH=5.90, 2. pH=3.90, 3. pH=1.50

equilibrium between two kinds of species. The spectrum for pH=5.9 of Fig. 2 coincides with that for pH=6.10 of Fig. 1, whereas the positions of the isosbestic points and the band shape of Fig. 2 (the acid solution) are different from those of Fig. 1 (the alkaline solution). This indicates, therefore, that the kinds of chemical species in the alkaline and the acid solution are different from each other.

With an increase in the acidity below pH=1.5, the spectral change appears again——that is, by increasing the concentration of sulfuric acid by at least from 9N to 27N, for instance, the spectrum is made to change with another set of isosbestic points. In this case, each absorption band for pH=1.50 of Fig. 2 behaves as follows. The 318 mμ band decreases in intensity, the 333 mμ band increases in intensity and shows a slight blue shift, and the 248 mμ band is only intensified, without any shift. According to the results for HDA-1, it is evident that four different kinds of species exist respectively as a stable one in four pH regions, including the strong acid and alkaline states (i.e., the extended

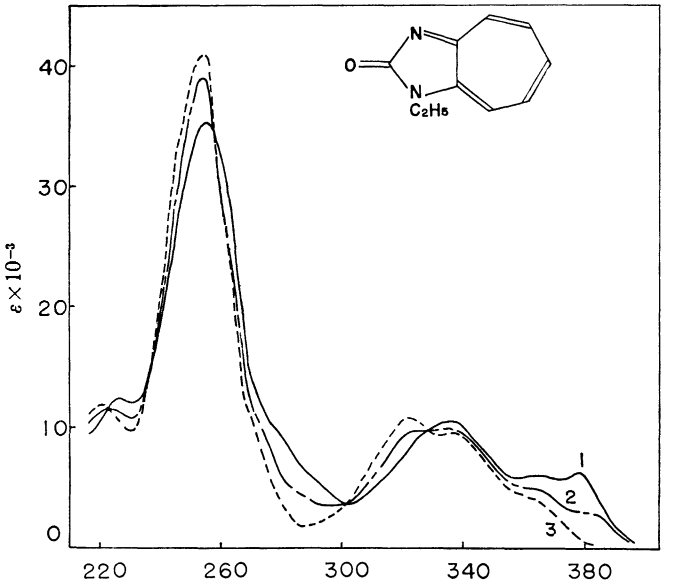

Fig. 3. Absorption spectra of (EDA-1) in aqueous acid solutions.
1. pH=5.85, 2. pH=4.01, 3. pH =1.85

pH region more than 12, the neutral state, at about the pH value of 1.5, and the strong acid state).

Figure 3 illustrates the absorption spectra of 1-ethyl-1,3-diazaazulene-2-one (abbreviated to EDA-1) in aqueous solutions from neutral to weak acid with various pH values. In addition, the spectrum of EDA-1 in an alkaline solution with a pH lower than 12.4 did not differ from that for pH=5.85 shown in Fig. 3. The behavior of the spectral change and the interval of acidity for the spectral change of EDA-1 correspond well with those in the case of HDA-1, though the absorption bands of the former are slightly longer in wavelength as a whole and are stronger in intensity than the corresponding bands of the latter. The correlation of the spectra of HDA-1 and EDA-1 in a strong acid solution is similar to that in a weak acid solution.

Consequently, in the case of EDA-1, there are a total of three kinds of species, each in one of three regions: neutral to alkaline, about pH=1.9, and strong acid.

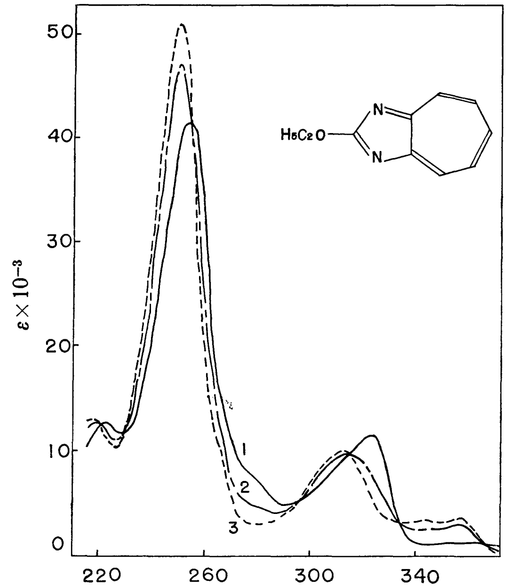

Fig. 4. Absorption spectra of (EDA-2) in aqueous acid solutions.
1. pH=5.62, 2. pH=3.30, 3. pH=1.88

Figure 4 represents the absorption spectra of 2-ethoxy-1,3-diazaazulene (abbreviation EDA-2) under conditions similar to those in Fig. 3. This sample did not show any appreciable change in spectra over the range from neutral to pH=11.9. In the strong acid solution, however, the sample showed a spectral change with the time dependence when the amount of added sulfuric acid was small, but the change was instantaneously completed when the amount was large. The resultant spectrum in either case coincided with that of HDA-1 in the strong acid solution. This suggests that EDA-2, which is stable in weak acid, is decomposed by strong acid and then becomes a species identical with that of HDA-1 in strong acid.

Accordingly, EDA-2 can exist as two independent species; one in the range from neutral to alkaline, and the other in the weak acid solution at about pH=1.90.

Calculation

The calculations were carried out by the semi-empirical method of LCAO-ASMO-SCF,[13] making use of the approximations by Pariser-Parr[14] and Nishimoto-Mataga [15] and the configuration interaction (CI). The geometry and the numbering of the atoms for 2-ethoxy-1,3-diazaazulene are shown in Fig. 5, in which the lengths of all C-C and C-N bonds are taken as 1.40Å. and in which that of C-O is taken as 1.41Å. The respective coordinates are listed in Table 1. For 1,3-diazaazulene, the same coordinates as above are taken, excluding the oxygen atom.

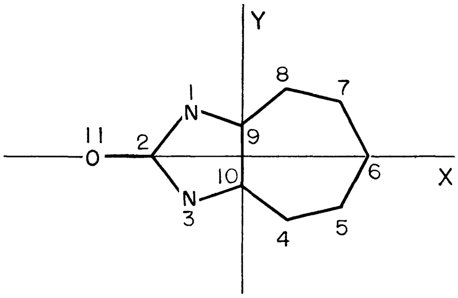

Fig. 5. Geometrical and numbering system for the 2-ethoxy-1,3-diazaazulene molecule.

For the Hückel MO calculation, the Coulomb integrals (α) and the resonance integrals (β) are used as follows:

$$\alpha_O = \alpha_C + 0.6\beta \qquad \beta_{CO} = 0.7\beta$$
$$\alpha_N = \alpha_C + 0.6\beta \qquad \beta_{CN} = 1.0\beta$$
$$\alpha_{C'} = \alpha_C + 0.1\beta$$

where $\alpha_C$is the Coulomb integral of the carbon atom, where β is the resonance integral between the adjacent carbon atoms, where the subscript O or N indicates oxygen or nitrogen respectively, and where C′ indicates the carbon atom adjacent to oxygen or nitrogen.

The one-center integrals are evaluated by the Pariser-Parr's equation. The parameters employed here are summarized in Table 2. The SCF calculations were repeated ten times, and a satisfactory convergence was obtained for the respective AO

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13) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 61 (1951).

14) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).

15) K. Nishimoto and N. Mataga, *Z. Phys. Chem. N. F.*, **13**, 140 (1957).

TABLE 1. COORDINATE FOR 2-ETHOXY-1,3-DIAZAAZULENE

Number of atom	X-coordinate	Y-coordinate
1	−1.33	1.13
2	−2.15	0.00
3	−1.33	−1.13
4	1.09	−1.57
5	2.46	−1.26
6	3.07	0.00
7	2.46	1.26
8	1.09	1.57
9	0.00	0.70
10	0.00	−0.70
11	−3.56	0.00

TABLE 2. PARAMETER VALUES USED

	C	O	N
Ionization potential (eV)	11.42	33.0	27.525
Electron affinity (eV)	0.58	11.48	13.435

	C-C	O-O	N-N
Core resonance integral (eV)	−2.236		
Const. in N.-M. eq.[a] (Å)	1.328	0.699	1.002

	C-O	C-N	O-N
Core resonance integral (eV)	−2.12	−2.576	
Const. in N.-M. eq.[a] (Å)	0.889	1.115	0.808

a) Nishimoto-Mataga's equation

coefficients. In the CI calculations, taking into account the SCF orbital energies, we considered the upper three occupied orbitals and the lower four unoccupied ones, and all the one-electron excitations were taken into account.

Table 3 represents the results for 1,3-diazaazulene and 2-ethoxy-1,3-diazaazulene. In the same table the results for azulene[10)] are added for comparison. According to Table 3, it can be seen that both azulene and 1,3-diazaazulene have five electronic transitions in the region below 50000 cm^{-1} (above 200 mμ), and that every transition of 1,3-diazaazu-

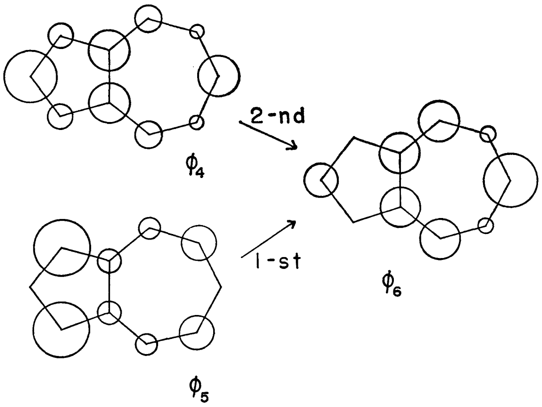


Fig. 6. Change in charge density associated with the transitions of $\Phi_5 \rightarrow \Phi_6$ and $\Phi_4 \rightarrow \Phi_6$ which are representative of the first and second transitions of 1,3-diazaazulene, respectively. Notice that the charge at 1 and 3 of Φ_5 and Φ_4 becomes zero in Φ_6.

TABLE 3. CALCULATED RESULTS FOR 1,3-DIAZAAZULENE AND 2-ETHOXY-1,3-DIAZAAZULENE

	Transition energy	Oscillator strength	Direction[a)]	Assignment
azulene[b)]	14798 cm^{-1}	0.026	90°	
	26667	0.007	0	
	34381	0.116	90	
	36644	1.787	0	
	45268	0.928	90	
	49328	0.026	0	
1,3-diazaazulene	21524	0.026	90	
	30445	0.062	0	
	35327	0.140	90	
	39966	1.743	0	
	45959	0.778	90	
	51336	0.247	0	
2-ethoxy-1,3-diazaazulene	22338	0.014	90	380 mμ band
	28338	0.215	0	330
	33917	0.210	90	290
	39649	1.802	0	260
	45603	0.654	90	230
	51130	0.181	0	

a) Angle of transition moment against X-axis
b) Taken from Ref. 10.

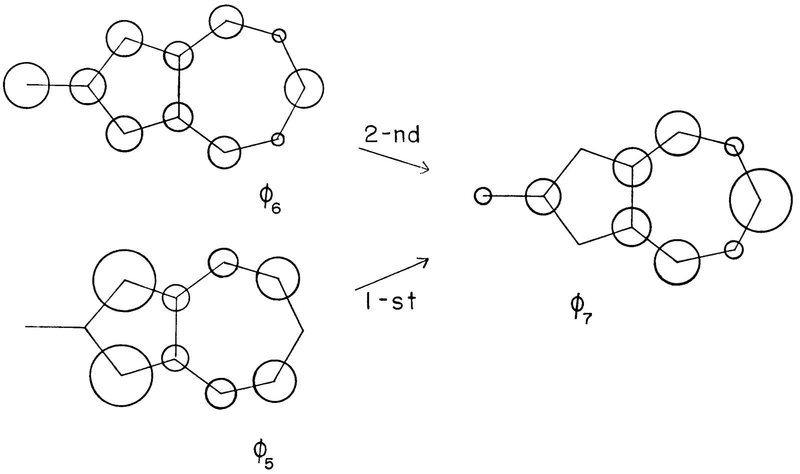


Fig. 7. $\Phi_5 \rightarrow \Phi_7$ and $\Phi_6 \rightarrow \Phi_7$ are representative of the first and second transitions of 2-ethoxy-1,3-diazaazulene (See, Fig. 6).

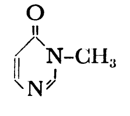
lene has larger wave numbers than that of azulene. This fact may be interpreted as follows. The magnitudes of the respective AO coefficients of the LCAO-MO's which are representative of the first and the second transitions, *i.e.*, $\Phi_5 \rightarrow \Phi_6$ and $\Phi_4 \rightarrow \Phi_6$ respectively, are shown diagrammatically in Fig. 6, where Φ_i represents the LCAO-MO and in which the subscript is the number in the order of increasing energy. According to Fig. 6, the change in the charge density at the positions 1 and 3 associated with the transitions $\Phi_5 \rightarrow \Phi_6$ is very large: that is to say, the large densities at 1 and 3 in Φ_5 and Φ_4 become exceedingly small in Φ_6, which is a representative MO of the excited states. Also, in the case of azulene, the corresponding transitions have the same character as above. However, the ionization potentials or the electron affinities at the positions 1 and 3 of azulene are small relative to those of 1,3-diazaazulene, because of the difference between carbon and nitrogen. Therefore, such a transition as $\Phi_5 \rightarrow \Phi_6$ or $\Phi_4 \rightarrow \Phi_6$ of 1,3-diazaazulene would need higher energies and appear at larger wave numbers than those of azulene. The same situations occur in connection with the other transitions.

2-Ethoxy-1,3-diazaazulene also possesses five electronic transitions in the range lower than 50000 cm^{-1} (above 200 mμ). The effect of the $-OC_2H_5$ substituent at the position 2 causes the first and the fifth transitions of 2-ethoxy-1,3-diazaazulene to shift to shorter wavelengths, and the rest to longer wavelengths relative to 1,3-diazaazulene. Moreover, the oscillator strengths of the second, the third, and the fourth transitions are increased, and the others are decreased, by the effect of $-OC_2H_5$. As above, the $-OC_2H_5$ substituent can cause some changes in the transition energies and oscillator strengths, but it cannot change the transition directions.

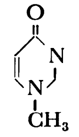
From a comparison of Figs. 6 and 7, it can be seen that the $-OC_2H_5$ group does not perturb the first and the second transitions. Especially, the character of the $\Phi_5 \rightarrow \Phi_7$ of 2-ethoxy-1,3-diazaazulene is almost the same as those representative of the first transitions of azulene and 1,3-diazaazulene.

Discussion

1. Chemical Structure. The three positions of protonation for HDA-1 or EDA-1 are considered to be aza nitrogen, amino nitrogen, and oxygen. Incidentally, a similar situation holds in the cases of the protonation of 1,6-dihydro-1-methyl-4-oxypyrimidine (expression (a), below) and 1,4-dihydro-1-methyl-4-oxypyrimidine (expression (b)).



(a)



(b)

Brown *et al.*[16] have considered that a protonation occurs at the aza nitrogen atom, because the spectra of the protonated species of (a) and (b) are similar to each other.

The mechanism of the protonation to HDA-1 and EDA-1 may be different from the cases of (a) and (b). In the present case, however, let us assume that the order of the ability as the proton acceptor of the functional groups of HDA-1 and EDA-1 is similar to those of (a) and (b); that is to say, let us assume that the first protonation occurs at the aza nitrogen rather than at amino nitrogen or oxygen.

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[16] D. J. Brown, E. Hoerger and S. F. Mason, *J. Chem. Soc.*, **1953**, 331.

As has been shown in the "Experimental" section, all the absorption patterns over the range of 200 mμ to 300 mμ are similar to one another; no characteristic difference among them appears until above 300 mμ. For that reason, let us examine the absorption bands which appear above 300 mμ in comparing the spectra.

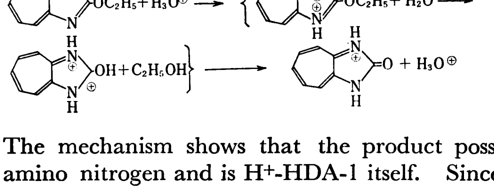
Murata[6] has considered that the system expressed by Eq. (1) contains HDA-1 as the main component, for the absorption pattern of the system is similar to that of EDA-1. It is natural that the electronic spectra associated with the π–π^* transitions of HDA-1 and EDA-1 are similar to each other, since they are isolectronic with respect to the π electron system. If some differences appear between the absorption patterns, it can be attributed to the difference in the substituents, –H and $-C_2H_5$. In fact, his consideration can be said to be reasonable, for the absorption spectra of HDA-1 (curve 1, Fig. 1) and EDA-1 (curve 1, Fig. 3) correspond to each other well.

We can now summarize our several results as follows. The temperature dependence of the spectrum of HDA-1 is as small as that of azulene, for which a tautomerism cannot be considered. HDA-1 and also EDA-1 can exist as independent species. HDA-1 in the neutral solution is not considered to be protonated, since no spectral change is observed in the range from neutral to $pH=12$. Taking these facts into account, it can safely be said that the hydrogen atom H of HDA-1 must be linked with the nitrogen atom at the position 1 of the diazaazulene skeleton in the same manner as C_2H_5 of EDA-1. If HDA-1 exists as a single species of another type (HDA-2 in Eq. (1)), then the spectrum should be correspondent to that of EDA-2. No such correspondencies, however, recognized between the curve 1 of Fig. 1 and the curve 1 of Fig. 4.

If an equilibrium such as Eq. (1) is supposed, the HDA-2 species may be found in the acid or the alkaline solutions. Let us compare the absorption spectra of HDA-1 and EDA-1 in the acid solution and that of EDA-2 in the neutral solution. In the case of EDA-1, the proton addition upon an increase in the acidity is expected to take place at the aza nitrogen atom and to produce H^+-EDA-1, as has been mentioned at the beginning of this section. The spectrum of HDA-1 in the acid state (curve 3, Fig. 2) closely resembles that of H^+-EDA-1 (curve 3, Fig. 3) rather than that of EDA-2 in the neutral state (curve 1, Fig. 4). This indicates that HDA-1 is not isomerized to HDA-2, as in Eq. (1), but is protonated and becomes H^+-HDA-1, as in the case of H^+-EDA-1.

Next, let us discuss the chemical species in the alkaline solution. As has been pointed out, EDA-1 and EDA-2 exist as a single species in the range from the neutral to the alkaline state, while HDA-1 in the alkaline state takes a spectral species different from that in the neutral state. The spectra of the chemical species may be compared as follows. The spectrum of the species of HDA-1 in the alkaline solution (curve 3, Fig. 1) does not resemble either the curve 1 of Fig. 4 in the neutral solution of EDA-2 or the curve 1 of Fig. 3, which is identical with that of EDA-1 in the alkaline solution. It is especially remarkably different from the former. This indicates that the species of HDA-1 in the alkaline state does not take the structure corresponding to EDA-2; that is, no isomerism such as Eq. (1) takes place. Moreover, the spectrum of HDA-1 in the alkaline state is not similar to that of EDA-1. Taking into consideration the possibility that a dissociation in the reverse process of the protonation occurs because of the variation from neutral to alkaline, it is reasonable that H is taken off as a proton from the amino nitrogen of HDA-1 during the variation, in some way such as $\text{HDA-1}+OH^- \rightarrow \text{HDA-1}^- + H_2O$.

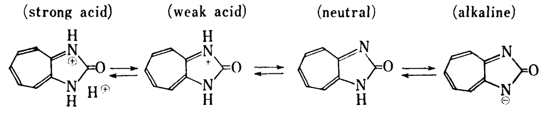
When HDA-1 is protonated and becomes H^+-HDA-1, the proton will go to aza nitrogen. This theory is strongly supported by the following facts. As has been pointed out in the "Experimental" section, in the process of the first protonation of EDA-2 a proton must go to either of two aza nitrogens, and H^+-EDA-2 is produced. If the second protonation occurred, the place to be attacked by a proton would be another aza nitrogen. In order to confirm this expectation, we carefully determined the second change in spectra upon the addition of sulfuric acid. The spectrum of the doubly-protonated species (H^+-EDA-2-H^+) gradually varied and became a spectrum coincident with that of H^+-HDA-1 in the weak acid solution. Upon the further addition of concentrated sulfuric acid, the spectrum of H^+-EDA-2-H^+ completely coincided with that of H^+-HDA-1-H^+ in the strong acid solution. The above results for the second protonation of H^+-EDA-2 include two important facts — that the resultant species loses the ethyl group and that it possesses amino nitrogen. In this case, the fact that the ethyl group is separated from H^+-EDA-2 in a strong acid state can be explained by the usual mechanism of hydrolysis by acid catalysis:



(2)

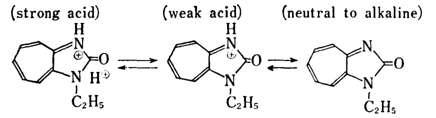
The mechanism shows that the product possesses amino nitrogen and is H^+-HDA-1 itself. Since the product shows an absorption pattern identical with that of H^+-HDA-1-H^+, the hydronium ion in the last expression of Eq. (2) may be attached as a proton to H^+-HDA-1 somewhere, but the exact position is not evident at the present stage. The mechanism also establishes that, in the first protonation-process for HDA-1, a proton must make an attack on the aza nitrogen atom at the position 3.

Conclusively, as for HDA-1 the chemical species which can exist over the whole region from strong acid to alkaline may be summarized as follows:

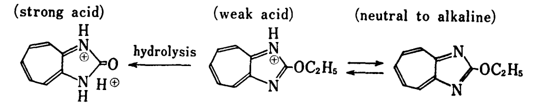


H^+-HDA-1-H^+ H^+-HDA-1 HDA-1 HDA-1^-

Also, the respective species considered with respect to EDA-1 and EDA-2 are;



H^+-EDA-1-H^+ H^+-EDA-1 BDA-1



H^+-HDA-1-H^+ H^+-EDA-2 EDA-2

2. Interpretation of the Spectra. The absorption spectrum of EDA-2 is shown in Fig. 8, as are, for the sake of comparison, the computed results. The correlation between the observed and the computed absorption bands with respect to number, location and intensity are satisfactory. The theoretical assignments of the bands are listed in Table 3. The transition energies of azulene and 1,3-diazaazulene in Table 3 have been computed taking larger values of the ionization energy and the electron affinity at the positions 1 and 3 for the latter than for the former. The resultant transition energies of 1,3-diazaazulene are always larger (at shorter wavelengths) than the corresponding ones of azulene.

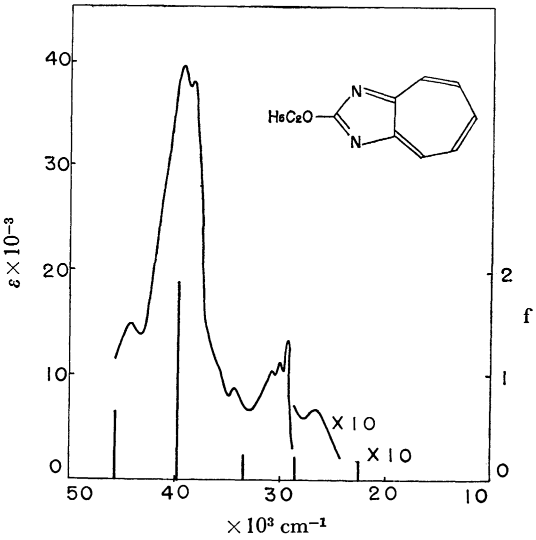


Fig. 8. Comparison of the calculated and observed (in cyclohexane) absorption bands of 2-ethoxy-1,3-diazaazulene, EDA-2.

In the case of protonation, the color bands of azobenzenes (*e.g.*, methyl-orange), for example, can remarkably shift to longer wavelengths.[17] On the contrary, in the present case, the protonation makes the π-π^* band shift to a shorter wavelength. When EDA-2 is protonated at the aza nitrogen atom and becomes H^+-EDA-2 the apparent increase in the ionization potential and the electron affinity of the nitrogen atom results. Therefore, if we take the larger ionization potential and electron affinity at either the 1 or 3 position for H^+-EDA-2, the resultant transition energies will become larger than those for EDA-2. Thus, the absorption bands of H^+-EDA-2 are at shorter wavelengths than the corresponding ones of EDA-2.

The absorption bands of H^+-HDA-1 and H^+-EDA-1 are located at shorter wavelengths, or at least not at longer ones, than the corresponding bands of HDA-1 and EDA-1 respectively. This can be explained in the same way as above. It should be noted here that an extra band peak appears at about 330 mμ, as illustrated in Fig. 2; at the present stage, however, we cannot assign that absorption. According to the dichroism analysis,[18] however, both of the 330 mμ peaks must belong to the second electronic transition, and so they are attributed to the fine structure. The first band of H^+-HDA-1 corresponding to the 370 mμ band of HDA-1 is the weak shoulder at about 360 mμ (curve 3, Fig. 2).

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