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The Structure of Certain Polyazaindenes. I. Absorption Spectra

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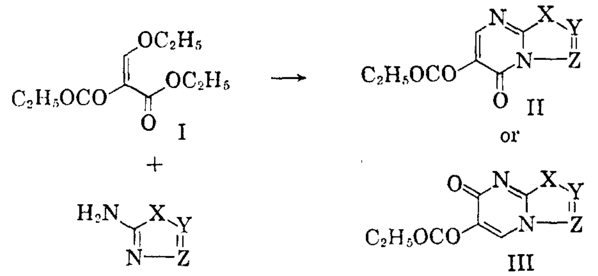
The structures of the polyazaindenes have been uncertain since their discovery many years ago, inasmuch as the syntheses are ambiguous, and no mild methods of degradation are available. The infrared and ultraviolet absorption spectra of a number of related heterocyclic ring systems are discussed. Structures are assigned based on the interpretation of the data.

The present paper is concerned with the interpretation of the ultraviolet absorption spectra of a large number of heterocyclic bases of related structures. The first part (A) deals with the condensation products of ethyl ethoxymethylenemalonate (I) with various heteroamines. The second part (B) covers the structure of the condensation products of ethyl acetoacetate with these same amines. Parts C and D are concerned with the thiadiazaindenes, the tetrazaindenes, and the pentazaindenes.

A. Carbethoxyazanaphthalenes and carbethoxyazaindenes. The substances (old and new) were prepared by condensing a number of heterocyclic amines having the amidino group, $-N{=}\overset{|}{C}-NH_2$, with ethyl ethoxymethylenemalonate (I) and ethyl acetoacetate. For instance, in a reaction involving I, X, Y, and Z may be nitrogen, sulfur, or carbon. The amines employed were 2-aminothiazoles, 2-amino-1,3,4-thiadiazoles, 5-amino-3-methyl-1,2,4-thiadiazole, 2-aminoimidazole, 3-amino-5-methyl-1,2-pyrazole, and 3-amino-1,2,4-triazoles. The reaction products of ethyl ethoxymethylenemalonate (I) with these amines and with certain alkyl derivatives are shown in Table I. The reaction failed with 5-aminotetrazole. As will become evident in the following discussion, the products have the oxo group in the position shown in II, rather than that in III.



The structures of 3-carbethoxy-4-oxo-4a-azanaphthalene (X)[1,2] and of 3-carbethoxy-4-oxo-1,4a-diazanaphthalene (XI),[3] which are isosteric with II, have been well established. These substances are taken as models with which to compare the spectra of derivatives of II. Inspection of Figs. 1 and 2 shows clearly that the shapes of the spectra of IV–IX are very similar to those of the two compounds (X and XI) of known structure.

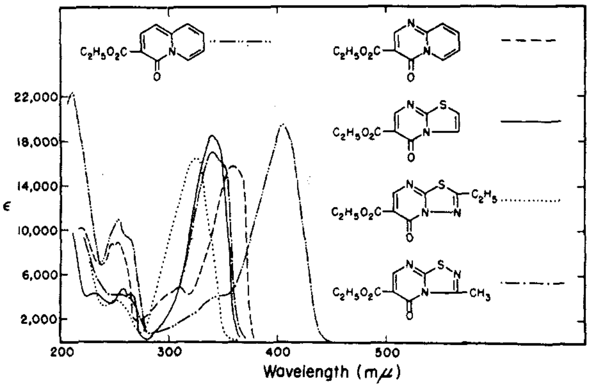


Fig. 1. Ultraviolet absorption spectra: IV, ———; V, ...; VI, -·-·-; XI, ———; X, ·-·-·-

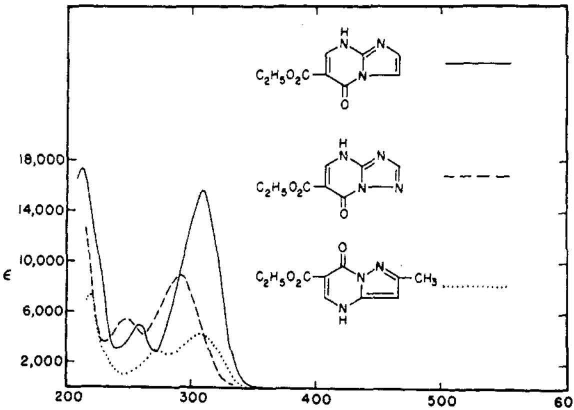


Fig. 2. Ultraviolet absorption spectra: VII, ———; VIII, ...; IX, ———

It is convenient, in discussing these spectra, to divide them into three regions: *a* (212–230 mμ) with high ε values, *b* (250–270 mμ) with medium ε

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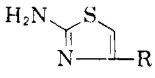
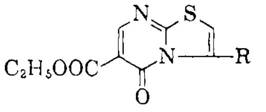
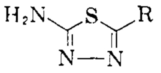
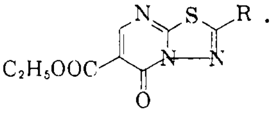
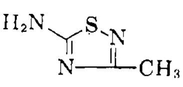
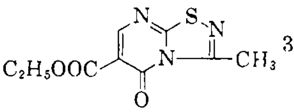
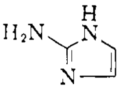
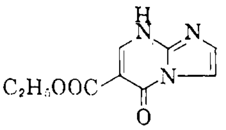
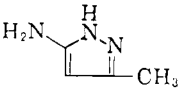
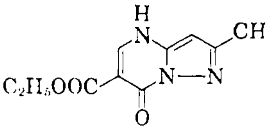
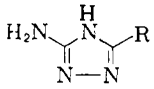
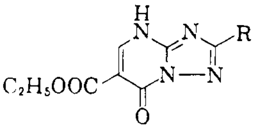
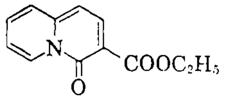
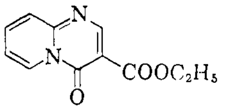
[1] F. Bohlmann, A. Englisch, J. Pollitt, H. Sander, and W. Weise, *Chem. Ber.*, **88**, 1831 (1955).

[2] V. Boekelheide and J. P. Lodge, Jr., *J. Am. Chem. Soc.*, **73**, 3681 (1951).

[3] R. Adams and I. J. Pachter, *J. Am. Chem. Soc.*, **74**, 5491 (1952).

TABLE I

ULTRAVIOLET ABSORPTION SPECTRA OF SOME HETEROCYCLIC OXOESTERS[a,b]

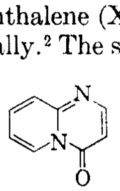
Amine Used	Product	5-Carbethoxy-4-oxo- Derivative of	No.	Absorption Bands λa	λb	λc	Δλc from X
		1-Thia-3a,7-diaza-indene	IV	236(4.1)	258(4.6)	340(18.6)	64
		3-Methyl-1-thia-3a,7-diazaindene	IVa		265(4.1)		
		2-Ethyl-1-thia-3,3a,7-triazaindene	V	215(10.7)	252(3.8)	324(16.5)	80
		2-Methyl-1-thia-3,3a,7-triazaindene	Va	218(9.7)	253(4.0)	322(15.4)	82
		3-Methyl-1-thia-2,3a,7-triazaindene	VI		260(5.7)	339(17.1)	65
		1,3a,7-Triazaindene	VII[c]	211(17.4)	258(5.0)	308(15.7)	96
		6-Carbethoxy-2-methyl-7-oxo-1,4,7a-triazaindene	VIII[c]	218(7.3)[d]	272(5.9)	306(4.1)	98
		1,3,3a,7-Tetraza-indene	IX[c]		248(5.1)	291(9.0)	113
		2-Methyl-1,3,3a,7-tetrazaindene	IXa[c]				
		3-Carbethoxy-4-oxo-4a-azanaphthalene	X	210(22.4)	253(11.0) 262(9.4) 248(4.1)	404(19.5)	
		3-Carbethoxy-4-oxo-1,4a-diazanaphthalene	XI	220(10.2)	248(8.8) 252(9.0) 310(5.0)	358(15.8)	46

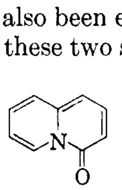
[a] In all tables, the wave length is given in mμ, and the extinction is $\epsilon \times 10^{-3}$. [b] The solvent was methanol. [c] A referee has suggested that these compounds should be named as 4,7-dihydro derivatives. We have chosen to omit this designation (1) in order to emphasize the relation to the derivatives in this table that have no other tautomers, since (2) the tautomeric hydroxy compounds are obviously completely unsaturated, (3) the rules covering specification of extra hydrogen specifically except cases of this sort, and (4) the name as given is unequivocal. [d] Incomplete solution.

values, and *c* (300–400 mμ) with high ε values. Table I shows that the *a* and *b* regions are relatively constant in position and intensity. Less fine structure is seen in the *b* region with increasing nitrogen content. The largest variation in these spectra occurs in the long wave-length band *c*. There is a hypsochromic shift of the *c* band as the ethylenic function in X is replaced successively by less efficient electrical conductors; thus, replacement of the carbon in the 1-position of X by a nitrogen atom, as in XI results in a hypsochromic shift of about 46 mμ and a corresponding decrease in intensity with respect to X. Similarly, substitution of a sulfur atom for the ethylenic function in the 7,8-position of X again results in a hypsochromic shift of about 64 mμ, as shown in IV. The pair V and VI are interesting in that position of a nitrogen atom relative to the sulfur atom has been changed. This affects the position of the long wave-length band, but does not alter the general shape of the absorption curve (Fig. 1). In VII, the ethylenic function in the 7,8-position of X has been replaced by a nitrogen atom. Here again, the nitrogen atom has caused the long wave-length band to be shifted about 96 mμ toward shorter wave lengths in respect to X. The isomeric compound, VIII, shows about the same absorption as VII. Increasing the nitrogen content of the molecule, as in IX, resulted in a further bathochromic shift of the long wave-length band, as shown in Fig. 2.[4]

These arguments, by analogy and from the fact that in no case was the spectrum similar to that of the type B compounds (see B), can be accepted as good evidence for Formulations IV through IX.

B. Azanaphthalenes and azaindenes. The structure of the condensation product of ethyl acetoacetate and 2-aminopyridine has been the subject of numerous papers and has been shown to be 4-oxo-1,4a-diazanaphthalene (XII).[2] The structure of 4-oxo-4a-azanaphthalene (XIII) has also been established unequivocally.[2] The spectra of these two substances


XII


XIII

will serve as reference spectra with which to compare the spectra of the condensation products of ethyl acetoacetate (or related esters) with the heterocyclic amines used in A.

The spectra of these compounds are shown in Figs. 3 and 4, and the values for the peaks of maximum absorption, together with their molecular extinction coefficients, are given in Table II.

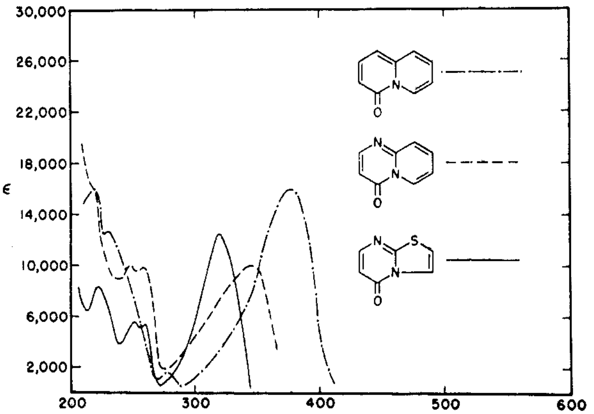


Fig. 3. Ultraviolet absorption spectra: XII, --------; XIII, -·-·-·-; XIV, ———

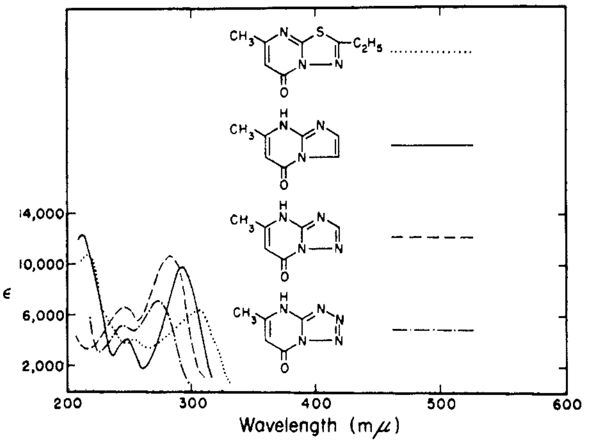


Fig. 4. Ultraviolet absorption spectra: XV, ...; XVI, ———; XVIII, --------; XIX, -·-·-·-

It is apparent, on comparison of Figs. 3 and 4 with Figs. 1 and 2, that there is a large hypsochromic shift of the entire spectrum between the two series, owing to the absence of the carbethoxy group. The general shape of the curves, however, remains unaltered. Furthermore, replacement of the 7,8-ethylenic group of XIII with sulfur or nitrogen has

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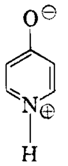
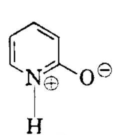
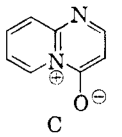
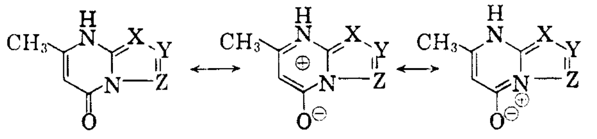
(4) V. I. Bliznyukov and V. M. Reznikov, *J. Gen. Chem. U.S.S.R.* (*Eng. Transl.*), **25**, 1735 (1955). These authors have shown, on the basis of spectral evidence, that 2- and 4-pyridones are most accurately represented by the formulations, A and B. If this condition obtains in the bicyclic heterocyclic examples, then a more accurate formulation of the foregoing substances is illustrated by C.

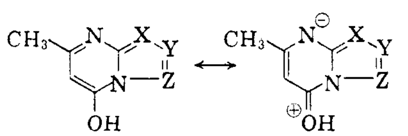

A


B


C

The anticipated spectrum of C should be reminiscent of naphthalene. The spectra of various substituted naphthalenes have been summarized by Morton and deGouveia [A. R. Morton and A. J. A. deGouveia, *J. Chem. Soc.*, p. 916 (1934)]. It is shown that their spectra fall into three regions, as follows: *a* about 220 mμ with high ε values; *b* 250–290 mμ with moderate ε values; *c* 295–325 mμ with low ε values. The *a* region has been identified as arising from the ethylenic chromophore and the *b* region from the styrene chromophore. It is seen immediately that there is a parallel between the spectra of naphthalene derivatives and the spectra of the compounds under discussion. This is good evidence that ionic structures would make important contributions to the resonance hybrid.

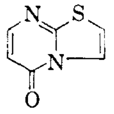
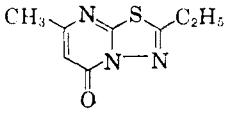
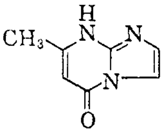
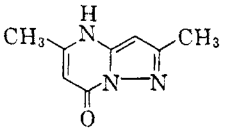
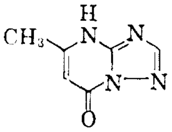
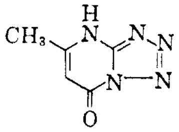

Formulation I


Formulation II

Formulation I is in better agreement with the infrared spectrum, which shows N—H absorption characteristic of an ammonium salt as a broad band at 3.6 to 4.0 μ and an amide carbonyl absorption at about 5.9 μ (not six-membered ring vibrations, which are unknown below 6.1 μ). The spectrum of 3,6-dimethyl-4-oxo-1,2,3a,7-tetrazaindene (Fig. 7) illustrates this point. (These absorptions do not enable us to distinguish between the 4- and 6-positions for the oxygen atom, but do show its carbonyl character. A different tautomer than that shown would also agree as well.)

TABLE II

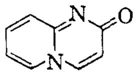
ULTRAVIOLET ABSORPTION SPECTRA OF SOME HETEROCYCLIC OXO BASES

	Substance	No.	Absorption Bands λa	 λb	 λc	Δλc from XIII
	4-Oxo-4a-azanaphthalene	XIII	220(16.0) 230(12.6)	277(1.6)	380(16)	
	4-Oxo-1,4a-diazanaphthalene	XII	220(16.0)	248(10.0) 258(9.6)	348(10.0)	32
	4-Oxo-1-thia-3a,7-diazaindene	XIV	220(8.4)	252(5.6) 260(5.4)	320(12.4)	60
	4-Oxo-6-methyl *derivatives of*					
	2-Ethyl-1-thia-3,3a,7-triazaindene	XV	215(10.8)	235(5.4) 255(4.1)	305(6.3)	75
	1,3a,7-Triazaindene	XVI	214(12.4)	248(4.2)	292(9.9)	88
	2-Methyl-3,3a,7-triazaindene	XVII	218(28.0)	255(6.4)[a]	292(6.8)	88
	1,3,3a,7-Tetrazaindene	XVIII		256(6.4)	278(10.8)	102
	Its 5-methyl isomer	XVIIIa		244(4.8)	280(9.0)	100
	1,2,3,3a,7-Pentazaindene	XIX		244(5.3)	274(6.3)	106

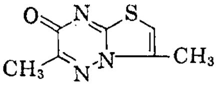
[a] In order to make this peak more obvious, this spectrum was run in ammoniacal methanol; this treatment causes little change in the position of the peaks of the other isomers.

resulted in a shift of the long wave-length band to shorter wave lengths, a result which parallels the carbethoxy derivatives previously described. The main absorption bands again fall roughly into three regions, as described for the first series. The chief difference is in the position of the long wave-length band which is now at shorter wave lengths with respect to XII and XIII. The similarities and differences between the two series will be seen more clearly by comparisons made from Tables I and II. It is apparent from consideration of these data that the long wave-length band is shifted progressively toward shorter wave lengths as the carbon atoms of the indene ring system are successively replaced by hetero atoms.

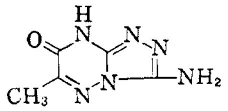
It might be argued that the alternate method of ring closure to give a structure of type III rather than II is responsible for the shorter wave-length absorptions of XVI through XIX. For this reason, three compounds: 2-oxo-1,4a-diazanaphthalene (XX), 3,5-dimethyl-6-oxo-1-thia-3a,4,7-triazaindene (XXI), and 3-amino-5-methyl-6-oxo-1,2,3a,4,7-pentazaindene (XXII)[5] were synthesized. These latter two substances may well be the 3,6-dimethyl-5-oxo-1-thia-3a,4,7-triazaindene and 3-amino-6-methyl-5-oxo-1,2,3a,4,7-pentazaindene isomers, respectively. In either case, the carbonyl group is connected to an exocyclic nitrogen atom, which is the relevant point for this discussion. Synthetic difficulties make the number of compounds for comparison in this series necessarily small.



XX



XXI



XXII

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[5] E. C. Taylor, Jr., W. H. Gumprecht, and R. F. Vance, *J. Am. Chem. Soc.*, 76, 619 (1954).

The structure of XX has been well established by Adams.[3] Its spectrum is shown in Fig. 5, together with the spectra of XXI and XXII. As is immediately apparent on comparison of Figs. 3 and 4 with Fig. 5, there is a considerable difference in the shapes of the absorption curves for the two series. The main difference is the relation of the long wave-length band in the *c* region to that of the absorption peak in the *b* region. In the II series (4-one), the ratio of the extinction coefficients of the *c* to that of the *b* band is always greater than 1, whereas, in the III (6-one) series, the *c* band is at best only one third the intensity of the *b* band. The relative intensities of these bands are shown in Table III. The values for XXI are included for comparison. Taking all the available evidence into account, the similarity of the absorption spectra of the condensation products described in this paper to those of the spectra of compounds with known II (4-one) configuration supports the thesis that the reaction of heterocyclic amines having the amidine structure $—N{=}\overset{|}{C}—NH_2$ with both ethyl ethoxymethylenemalonate and ethyl acetoacetate proceeds to give, as the principal products, compounds possessing the 4-one structure.

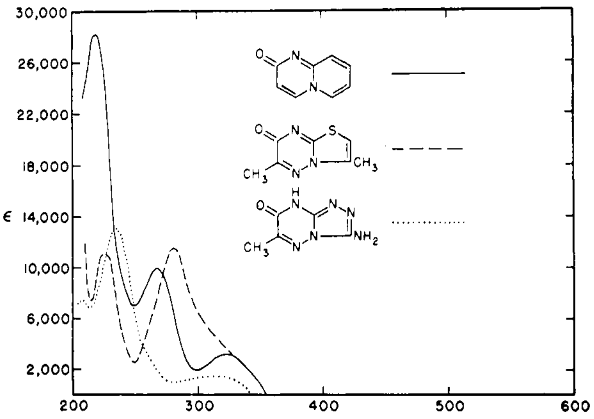


Fig. 5. Ultraviolet absorption spectra: XX, ———; XXI, – – – –; XXII, ...

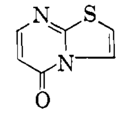
TABLE III

COMPARISON OF ULTRAVIOLET ABSORPTION DATA OF THE 4-*ONE* AND 6-*ONE* SERIES

Compound	λa	λb	λc	Intensity Ratio, $\frac{c}{b}$
XVI	214(12.4)	248(4.2)	292(9.9)	2.4
XX	218(28.2)	268(10.0)	324(3.2)	0.31
XXI	226(11.1)	280(11.6)	322(3.4)	0.29
XXII	218(7.4)	240(13.1)	310(1.4)	0.11

C. Thiadiazaindenes. A comparison of the ultraviolet absorption spectra of several derivatives of 4-oxo-1-thia-3a,7-diazaindene (XIV) may be of interest. The introduction of a methyl group into the 6-position of a thiadiazaindene nucleus, as in XIVa, produces a new band at 212 mμ and a splitting of the *c* band into a peak at 313 mμ and a shoulder at 323 mμ. An additional methyl group, as in 3,6-dimethyl-4-oxo-1-thia-3a,7-diazaindene (XIVb), again shows the 212 mμ band, and the *c* band has been split into two definite bands at 323 mμ and 338 mμ.

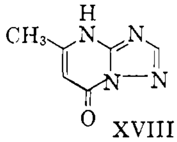
XIV. —
XIVa. 6-CH_3
XIVb. 3,6-diCH_3



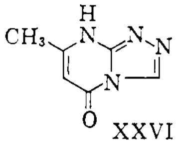
XXIII. 6-CH_3-3-C_6H_5
XXIV. 5-$CO_2C_2H_5$-3-C_6H_5
XXV. 5-$CO_2C_2H_5$-2-Cl

The 5-carbethoxy- (IV), the 5-carbethoxy-3-methyl- (IVa), and the 5-carbethoxy-3-phenyl- (XXIV) derivatives show a bathochromic shift of the long wave-length bands, as would be expected for the respective auxochromes. The *b* band in the spectrum of 5-carbethoxy-2-chloro-4-oxo-1-thia-3a,7-diazaindene (XXV) has almost disappeared, occurring only as a shoulder. The ultraviolet absorption data for this series are collected in Table IV.

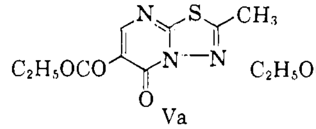
D. 1,2,3a,7- and 1,3,3a,7-Tetrazaindenes. 3-Amino-1,2,4-triazole reacts with ethyl acetoacetate and certain related substances to give a tetrazaindene, m.p. 278°, but an isomer, m.p. 254°, results when 2-hydrazino-4-hydroxy-6-methylpyrimidine is cyclized by warm formic acid.[6] The latter is isomerized to the former by treatment with hot formic acid. Both isomers show ultraviolet absorption spectra typical of a 4-one structure (Figs. 9 and 10); accordingly, the two structures (XVIII and XXVI) must be involved. It was shown in the related systems, Va and VI, that a shift of the nitrogen atom from the 3-position to the 2-position resulted in a bathochromic shift of about 17 mμ in the absorption of the long wave-length band (cf. Fig. 1, Table I). Since there is a 16-mμ difference in the long wave-length absorptions of the two isomers, structure XVIII has been assigned to the 278° isomer and XXVI to the 254° isomer.



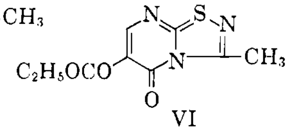
XVIII



XXVI



Va



VI

It is curious that both XVIII and XXVI show one acidic hydrogen when titrated against potassium methoxide in a nonaqueous titration, yet form

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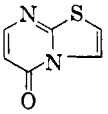
[6] C. F. H. Allen, H. R. Beilfuss, D. M. Burness, G. A. Reynolds, J. F. Tinker, and J. A. VanAllan, *J. Org. Chem.*, 24, 787 (1959).

TABLE IV

ULTRAVIOLET SPECTRA OF 4-OXO-1-THIA-3a,7-DIAZAINDENES



			Absorption Bands	
Compound	Substituent	λa	λb	λc
XIV	None	222(8.4)	252(5.6) 260(5.3)	320(12.5)
XIVa	6-CH_3	212(9.7) 225(11.4)	252(4.9) 260(4.8)	313(10.3) ~323
XIVb	3,6-di-CH_3	212(9.6) 231(10.0)	258(4.9) 265(4.8)	323(10.8) 338(9.4)
XXIII	6-CH_3-3-C_6H_5	228(8.0)	256(7.0) 280(6.3)	350(11.0)
IV	5-$CO_2C_2H_5$	336(4.1)	258(4.6) 261(4.1)	340(18.6)
IVa	5-$CO_2C_2H_5$-3-CH_3	243(5.7)	260(4.2)	348(16.6)
XXIV	5-$CO_2C_2H_5$-3-C_6H_5	222(11.2)	268(10.3)	352(15.6)
XXV	5-$CO_2C_2H_5$-2-Cl	232(6.9)	~258	342(17.4)

well-defined salts with methyl *p*-toluenesulfonate. The absorption spectra of these salts (Fig. 6) parallel those of the parent compounds in respect to the relative positions of the long wave-length bands. These latter bands have increased intensity and a short wave-length band has appeared in the 210–220 mμ region. Attention is drawn to the marked similarity of the absorptions of the salts to XIV, again emphasizing the 4-one structures.

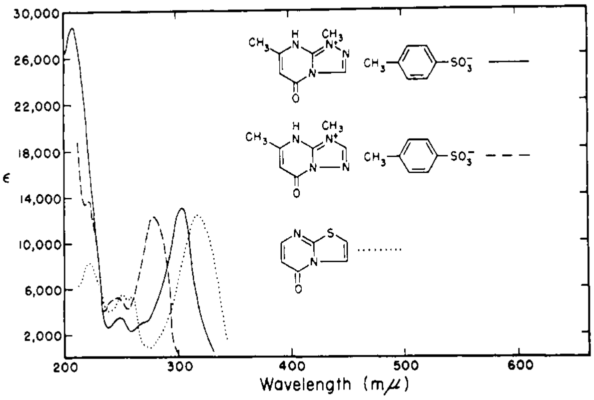
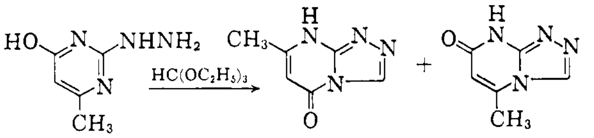


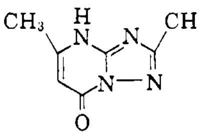
Fig. 6. Ultraviolet absorption spectra of two salts and XIV, ...

When 2-hydrazino-4-hydroxy-6-methylpyrimidine is treated with a nonacidic formylating agent (ethyl orthoformate, dimethylformamide), two isomeric tetrazaindenes are produced. One of these is identical with the isomer, XXVI, previously mentioned as having been obtained using warm formic acid. The second was also obtained from the same hydrazinopyrimidine and phenyl isothiocyanate; this reaction gave a mercapto derivative, in which the —SH group was replaced by hydrogen when catalytically reduced in the presence of Raney nickel.[6] The new isomer is 4-methyl-6-oxo-1,2,3a,7-tetrazaindene (XXVII).

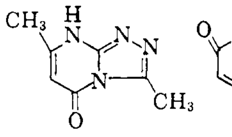


XXVI XXVII

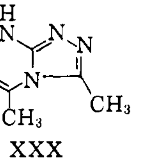
The dimethylhydroxytetrazaindenes (XXVIII–XXX) corresponding to the monomethyl series have been prepared by analogous reactions. The



XXVIII



XXIX



XXX

melting points of the three isomers are almost identical, and a mixture of the two 4-one isomers does not give a depressed melting point, whereas a mixture of 4-one and 6-one isomers does.[7]

Three of the four isomers theoretically possible from the reaction of 3-amino-1,2,4-triazole and ethyl acetoacetate have, thus, been prepared, along with the corresponding products from 3-amino-5-methyl-1,2,4-triazole. Numerous attempts to synthesize the fourth isomer in each series have met with failure. The ultraviolet spectra of these substances are collected in Table V. The ultraviolet spectrum of XXVII has a peak absorption at 248 mμ, which is consistent with the 6-one structure. The spectra of the dimethyl series, XXVIII, XXIX, and XXX, parallel exactly those of the monomethyl series, as shown in Table V. While the infrared spectra of XVIII and XXVI are about identical (see Figs. 9 and 10), there is considerable difference in their ultraviolet spectra. The infrared

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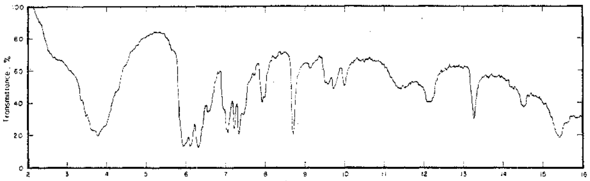
[7] C. F. H. Allen, H. R. Beilfuss, D. M. Burness, G. A. Reynolds, J. F. Tinker, and J. A. VanAllan, *J. Org. Chem.*, **24**, 793 (1959).

spectra of the 4-ones, XXIX and XXVIII, are quite similar but are not identical (see Figs. 7 and 8).

TABLE V

ULTRAVIOLET SPECTRA OF METHYL AND DIMETHYL OXOTETRAZAINDENES

Compound	λa	λb	λc
XVIII	210	256 (6.4)	278 (10.8)
XXVI	210 (17.7)	246 (4.8)	294 (6.8)
XXVII	210 (22.7)	248 (7.0)	
XXX	210 (23.0)	248 (6.6)	
XXIX	209 (17.0)	248 (4.6)	298 (9.2)
XXVIII	210 (23.5)	238 (2.8)	272 (9.5)



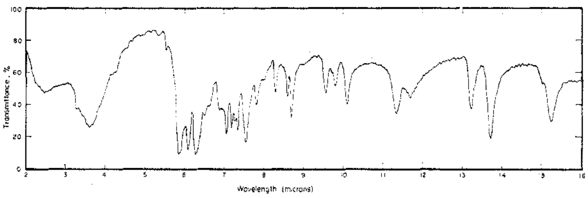
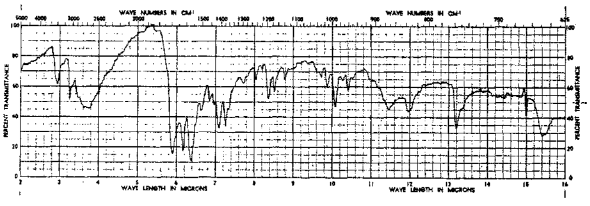


Fig. 7. Infrared spectrum of 3,6-dimethyl-4-oxo-1,2,3a,7-tetrazaindene (XXIX)

Fig. 8. Infrared spectrum of 2,6-dimethyl-4-oxo-1,3,3a,7-tetrazaindene (XXVIII)



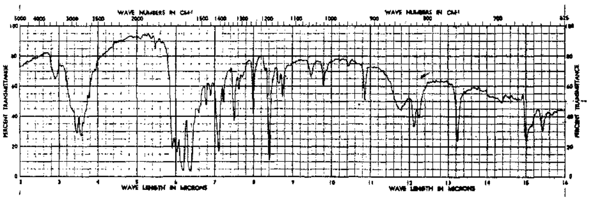


Fig. 9. Infrared spectrum of 6-methyl-4-oxo-1,2,3a,7-tetrazaindene (XXVI)

Fig. 10. Infrared spectrum of 6-methyl-4-oxo-1,3,3a,7-tetrazaindene (XVIII)

Attention is drawn to the remarkable similarity of spectra in the 6-one series. Thus, XXVII and XXX have very similar absorptions in the infrared (see Figs. 11 and 12), but they are greatly different from the isomeric 4-one series, particularly in the carbonyl region. The 4-one series has an amide band below 6 μ, whereas the 6-one series has a band at 6 μ. The large amount of fine-structure vibrations between 3 and 4 μ seems to be characteristic of the 6-one series.

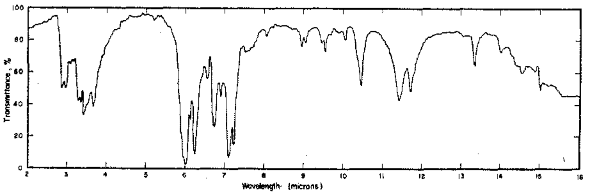


Fig. 11. Infrared spectrum of 3,4-dimethyl-6-oxo-1,2,3a,7-tetrazaindene (XXX)

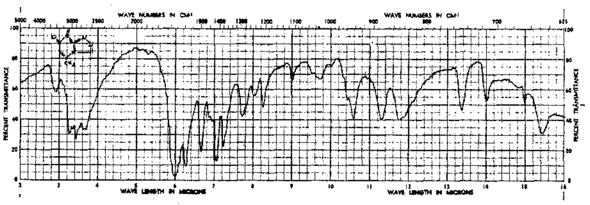
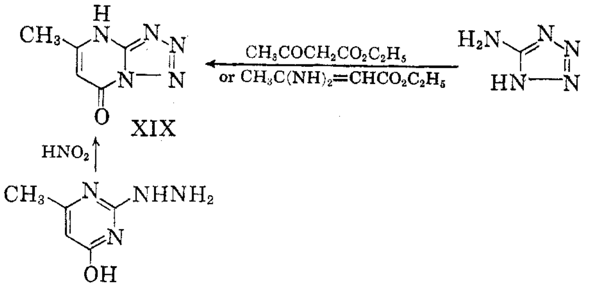


Fig. 12. Infrared spectrum of 4-methyl-6-oxo-1,2,3a,7-tetrazaindene (XXVII)

The condensation of 5-aminotetrazole with ethyl acetoacetate or with ethyl β-aminocrotonate gives a product (XIX) identical with that obtained by the action of nitrous acid on 2-hydrazino-4-hydroxy-6-methylpyrimidine.[7] Since the five-membered tetrazole ring is symmetrical, the only two possible isomers are 6-methyl-4-oxo- (XIX) and 4-methyl-6-oxo-1,2,3,3a,7-pentazaindene. In all known instances,[4,8] ethyl β-aminocrotonate has been shown to give compounds of the 4-one configuration. For this reason, it seems highly probable that XIX represents the correct configuration of the reaction product of the tetrazole with ethyl β-aminocrotonate.



The effect of substituents on the ultraviolet absorption spectrum of 4-oxo-1,3,3a,7-tetrazaindene (XXXI) is shown in Table VI. The *a* band occurs at wave lengths of less than 200 mμ and can be seen only in the salts (Fig. 6). The *b* band is relatively constant in position and intensity in the whole series. Methyl substituents as in XVIII and XVIIIa do not affect the *c* band, in contrast to the 1-thia-3a,7-diazaindene series. As the 2-position is progressively substituted by more efficient electron donors, the long wave-length band is shifted

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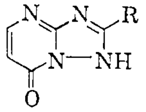
[8] H. Antaki and V. Petrow, *J. Chem. Soc.*, 551 (1951).

toward longer wave lengths (IX through XXXV, Table VI). It is clear then, that these substituents are attached to the end of a conjugated system, such as is indicated in XXXVI.



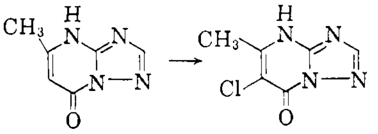
XXXVI

TABLE VI

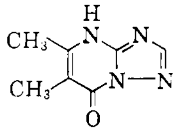
ULTRAVIOLET ABSORPTION SPECTRA OF 4-OXO-1,3,3a,7-TETRAZAINDENES

Compound	Substituent	λb	λc
XXXI		248 (10.8)	282 (12.9)
XVIII	6-CH_3	256 (6.4)	278 (10.8)
XVIIIa	5-CH_3	244 (4.8)	280 (9.0)
XXXII	6-Me-5-Cl	262 (7.2)	298 (10.8)
IX	5-$CO_2C_2H_5$	247 (5.3)	290 (8.9)
IXa	5-$CO_2C_2H_5$-2-CH_3	248 (5.4)	291 (9.0)
XXXIII	5-$CO_2C_2H_5$-2-CH_2OH	252 (5.8)	298 (10.0)
XXXIV	5-$CO_2C_2H_5$-2-SCH_3	265 (6.6)	308 (16.2)
XXXV	5-$CO_2C_2H_5$-2-NH_2	252 (3.0)	310 (14.0)

Chlorination of XVIII gives the 5-chloro derivative (XXXII),[6] but the position taken by the entering methyl group when methylation is effected by dimethyl sulfate is unknown. It is probably on one of the nitrogen atoms, because of a negative Zeisel (not oxygen alkylation); carbon alkylation is excluded since the substance is not identical with the known isomer, XXXVII.[9] From the absorption spectra it is apparent that the -one structure of XVIII is still present (Table VII).

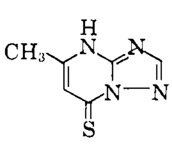


XVIII XXXII

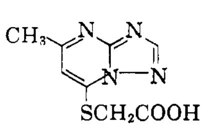


XXXVII

The sulfur analog[8] of XVIII has an ultraviolet spectrum comparable in respect to shape, showing that it, too, has the thiono structure (XXXVIII). When this substance is alkylated by sodium



XXXVIII



XXXIX

chloroacetate, the alkylation product shows a hypsochromic shift of 40 mμ in the long wavelength band (Table VII). This indicates the disappearance of the thiono structure, i.e., S-alkylation has occurred to give XXXIX.

The 4-chloro- and 4-amino-derivatives (XL and XLI), as well as XXXIX, resemble the parent base (XLII), having quite similar spectra, with the expected modifications due to the substituents (Table VII).

TABLE VII

ULTRAVIOLET ABSORPTION SPECTRA OF MISCELLANEOUS 1,3,3a,7-TETRAZAINDENES

Compound	Substituent	λ max b	λ max c
XVIII	6-CH_3-4-oxo	256 (6.4)[a]	278 (10.8)
XXXII	6-CH_3-5-Cl-4-oxo	262 (7.2)	298 (10.8)
XXXVII	5,6-$(CH_3)_2$-4-oxo	265 (4.7)	298 (12.5)
XXXVIII	6-CH_3-4-thiono	235 (9.0)	336 (20.8)
XXXIX	6-CH_3-4-SCH_2CO_2H	210 (15.0)[b]	291 (11.4)
XL	6-CH_3-4-Cl	222 (23.8)[b]	272 (5.0)
XLI	6-CH_3-4-NH_2		288 (13.5)
XLII	6-CH_3	234 (1.5)	271 (4.0)

[a] Run in ammoniacal methanol. Lacking a 5-substituent, XVIII shows a very faint *b* band in neutral or acidic methanol; see footnote *a*, Table II. [b] These are λa bands.

EXPERIMENTAL

The various new substances were mostly prepared by one of the following general procedures. Their properties are collected in Table VIII.

A. Equimolecular quantities of the heterocyclic amine and ethyl acetoacetate or ethyl ethoxymethylenemalonate in 5 volumes of trichlorobenzene were refluxed and the ethanol was collected until the theoretical amount had been evolved. The reaction mixture was cooled and the solid collected. In some cases, it was necessary to add petroleum ether to the cooled reaction mixture to precipitate the product. The solid was washed with petroleum ether and recrystallized from the appropriate solvent.

B. A mixture of the amine and 10% excess of either of the esters in 3 to 5 volumes of acetic acid was refluxed 3–6 hr. and cooled. If a solid separated, it was collected and recrystallized. In some cases, it was necessary to concentrate the reaction mixture to obtain the product.

C. A solution of 0.1 mole of the carbethoxyindene in 150 ml. of 2*N* hydrochloric acid was refluxed for 5 hr., cooled, and the solid collected and recrystallized.

D. A mixture of the amine and a 10% molar excess of ethyl β-aminocrotonate was held at 180–190° for 8 hr. If the product was a low-melting solid, for example, XV, the reaction mixture was subjected to vacuum distillation. Otherwise, alcohol was added and the product was collected on a filter.

3,5-Dimethyl-6-oxo-1-thia-3a,4,7-triazaindene (XXXI). A mixture of 0.02 mole each of 3-amino-2-imino-4-methylthiazoline hydrochloride[10] and pyruvic acid in 50 ml. of 2*N* sulfuric acid was refluxed 4 hr. and evaporated *in vacuo* to 6 ml. The residue was carefully neutralized with 3*N* sodium hydroxide solution and the solid collected and recrystallized from water. Yield, 3 g. of the indene, m.p. 227°.

Anal. Calcd. for $C_7H_7N_3OS$: N, 23.2; S, 17.7. Found: N, 23.2; S, 17.3.

Acknowledgment. We are indebted to Dr. D. W. Stewart and Miss T. J. Davis, of these Laboratories, for the ultraviolet and infrared spectra.

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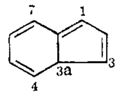
(9) E. Birr, *Z. wiss. Phot.*, **50**, 107 (1955).

(10) H. Beyer, W. Lassig, and E. Bulka, *Ber.*, **87**, 1385 (1954).

TABLE VIII

PROPERTIES OF POLYAZAINDENES



No.	Substituents and Positions	Method of Prep.	M.P., °C.	Empirical Formula	Analysis Calcd. % C	Calcd. % H	Calcd. % N	Found % C	Found % H	Found % N
4-Oxo-1-thia-3a,7-diazaindenes										
IV	5-COOC$_2$H$_5$[a]	A	186	$C_9H_8N_2O_3S$	48.4	3.5		48.3	3.5	
IVa	5-COOC$_2$H$_5$-3-CH$_3$[b]	A	192	$C_{10}H_{10}N_2O_3S$	50.5	4.1		51.8	5.1	
IVb	5-COOH	C	285 dec.	$C_7H_6N_2O_4S$	39.2	2.8		39.0	2.6	
XIV	None[c]	[d]	116	$C_6H_4N_2OS$	47.3	2.6		47.3	2.9	
XIVa	6-CH$_3$[c]	B	112	$C_7H_6N_2OS$	50.6	3.6		50.3	3.9	
XIVb	3,6-(CH$_3$)$_2$[e,f]	D	133–135	C_8H_8NOS						
XXIII	6-CH$_3$-3-C$_6$H$_5$[g]	B	238–240	$C_{13}H_{10}N_2OS$	64.5	4.5		63.4	4.3	
XXIV	5-COOC$_2$H$_5$-3-C$_6$H$_5$[a]	A	174	$C_{14}H_{12}N_2O_3S$	60.0	4.0		60.1	4.1	
XXV	5-COOC$_2$H$_5$-2-Cl[b]	A	149	$C_9H_7ClN_2O_3S$	41.8	2.7		42.0	2.7	
	5-COOC$_2$H$_5$-3-C$_6$H$_5$C$_6$H$_4$[b]	A	169	$C_{21}H_{16}N_2O_3S$	66.0	4.4		66.8	4.3	
	5-COOC$_2$H$_5$-3-NO$_2$[h]	A	225	$C_9H_7N_3O_5S$	39.4	2.5		39.4	2.9	
4-Oxo-1-thia-3,3a,7-triazaindenes										
V	5-COOC$_2$H$_5$-2-C$_2$H$_5$[g]	A	96	$C_{10}H_{11}N_3O_3S$	47.5	4.3		47.6	4.6	
Va	5-COOC$_2$H$_5$-2-CH$_3$[a]	A	140	$C_9H_9N_3O_3S$	45.2	3.8		45.2	3.6	
XV	2-C$_2$H$_5$-6-CH$_3$[c]	D	40	$C_8H_9N_3OS$	49.2	4.6		49.0	4.7	
4-Oxo-1-thia-2,3a,7-triazaindene										
VI	5-COOC$_2$H$_5$-3-CH$_3$[c]	A	110	$C_9H_9N_3O_3S$	45.2	3.8	17.5	45.3	3.6	17.6
4-Oxo-1,3a,7-triazaindenes										
VII	5-COOC$_2$H$_5$[i]	B	253	$C_9H_9N_3O_3$	52.2	4.4	20.3	52.4	4.3	20.6
XVI	6-CH$_3$[i]	B	239	$C_7H_7N_3O$			28.2			27.8
7-Oxo-1,4,7a-triazaindenes										
VIII	2-CH$_3$-6-COOC$_2$H$_5$[j]	B	294	$C_{10}H_{11}N_3O_3$			19.0			18.7
XVII	2,5-(CH$_3$)$_2$[j]	B	253	$C_8H_9N_3O$	58.5	5.5	25.8	59.4	6.5	26.3
	2-CH$_3$-5-C$_6$H$_5$[j]	B	286	$C_{13}H_{11}N_3O$			18.6			19.3
	5-CH$_3$-2-C$_6$H$_5$[j]	B	>315	$C_{13}H_{11}N_3O$	69.3	4.9	18.6	69.8	5.0	19.6
	5-CH$_3$[j]	B	307	$C_7H_7N_3O$	56.4	4.7	28.2	56.0	4.8	28.6
	2-CH$_3$-6-COOH	C	>285 dec.	$C_8H_7N_3O_3$	49.7	3.6		49.4	4.0	

[a] Recrystallization from ethanol. [b] Butanol. [c] Ligroin. [d] Decarboxylation of IVb. [e] H. Antaki and V. Petrow, *J. Chem. Soc.*, 551 (1951). [f] Benzene-ligroin. [g] Toluene-ligroin. [h] Ethyl nitrate. [i] Water. [j] Dimethylformamide.

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The Structure of Certain Polyazaindenes. II. The Product from Ethyl Acetoacetate and 3-Amino-1,2,4-triazole

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3-Amino-1,2,4-triazole and ethyl acetoacetate or diketene give only one of the four possible isomeric substances, which is 6-methyl-4-oxo-1,3,3a,7-tetrazaindene. Two of the other isomers are obtained from 2-hydrazino-4-methyl-6-hydroxypyrimidine and ethyl orthoformate. One of the latter is isomerized to the first substance by strong acid. A number of related compounds are described and their interrelationships are shown. The accumulated spectral and chemical evidence support the structure named; the latter is also in accord with theoretical considerations.

In a study of the reaction between aminotriazoles and 1,3-dicarbonyl compounds, Bülow[1,2] obtained a substance from 3-amino-1,2,4-triazole and ethyl acetoacetate to which he assigned the structure Ia, 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene.[2,3] Since the structure was not determined by the method of synthesis, it was assumed that the

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(1) C. Bülow, *Ber.*, **42**, 2599, 3555, 4429 (1909).

(2) C. Bülow and K. Haas, *Ber.*, **42**, 4638 (especially, p. 4642)(1909).