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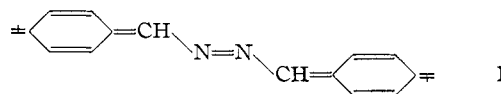
Absorption Spectra. IV. Ketazines¹

BY ELKAN R. BLOUT, VIRGINIA W. EAGER AND RALPH M. GOFSTEIN

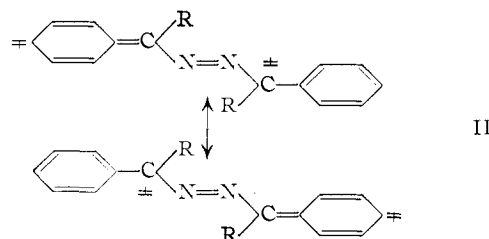
Recently,² the absorption spectra of several aromatic aldazines have been determined and certain structural features have been correlated with the spectra. In this communication we wish to present the results of some further studies upon the spectra of azines, particularly those of aromatic ketones and the mixed azines from aromatic ketones and aromatic aldehydes.

Azines derived from saturated aliphatic ketones, such as acetone, show absorption only in the far ultraviolet, below 240 $m\mu$. As soon as one or more aromatic groups are introduced into the azine molecule, the absorption is shifted toward longer wave lengths, which allows for easy measurement by the ultraviolet spectrophotometer. The effect of alkyl substitution on the α and α' carbon atoms of the simplest aromatic azine, benzalazine, is shown in Fig. 1. This compound, as has already been pointed out,² has a single, intense absorption peak at 300 $m\mu$. The effect of α -alkyl substitution in benzalazine is to shift the absorption maximum toward shorter wave lengths as can be observed from the spectrum of benzaldehyde-acetophenone azine³ which shows a maximum at 278 $m\mu$. Further enhancement of this effect may be observed in the spectra of acetophenone azine in which the absorption maximum has been shifted toward still shorter wave lengths and lies at 267 $m\mu$. A similar shift in absorption has been noted by Jones⁴ in the spectra of methyl substituted *trans* stilbenes. Jones correlated the shift of the absorption spectrum maximum with the steric configuration and lack of coplanarity of the molecules. In the case of the azines discussed herein, this may be a contributing effect, but probably not the only operative effect, since benzaldehyde-acetophenone azine and acetophenone azine may show coplanar structures⁵ which the methyl stilbenes cannot. It is interesting to note that the introduction of larger alkyl groups such as those in propiophenone azine or α -tetralone azine seem to have little additional effect upon the spectra (Fig. 1). Both

of these compounds show one maximum *ca.* 270 $m\mu$ and one maximum (or an inflection point) *ca.* 300 $m\mu$. The significant point about the spectra of the above-mentioned α, α' -dialkyl substituted benzalazines is that they seem to be made up of two absorbing units; the first is the linear benzalazine structure, whose absorption at 300 $m\mu$ may be correlated with transitions to excited states such as I



and the second is a structure absorbing at shorter wave lengths, *ca.* 270 $m\mu$, which is probably associated with forms such as II where one of the benzene rings is in a different plane from the other, due to the effect of the α -alkyl group.



Phenomena analogous to those observed with the isomeric hydroxybenzalazines are shown by the isomeric hydroxyacetophenone azines (Fig. 2). The *p*-hydroxy compound has a single maximum at 303 $m\mu$, a displacement of 36 $m\mu$ as compared with the unsubstituted azine. In the *m*-compound, two maxima are noted; the first at 268 $m\mu$, which is the same point at which the unsubstituted compound shows maximum absorption, and a second peak at 297 $m\mu$. In the *o*-hydroxylated compound, complete separation of the two maxima exists with their peaks at 293 and 362 $m\mu$, respectively. The spectra just described are in line with considerations already discussed² in connection with the linearity of the corresponding hydroxy-substituted benzalazines with provision, of course, for the effect of the alkyl substituents in the α and α' positions. The hydroxyl group in general has a bathochromic effect, since it tends to give up electrons to the aromatic group, and thus the absorption is shifted toward longer wave lengths than in non-hydroxylated compounds.

The effect of aromatic substitution in the α and α' positions of benzalazine was next studied (Fig. 3). The mixed azine prepared from benzophenone and benzaldehyde shows absorption in exactly the same region as the parent compound, which

(1) For the last paper in this series see Blout, Eager and Silverman, *THIS JOURNAL*, **68**, 566 (1946).

(2) Blout and Gofstein, *ibid.*, **67**, 13 (1945).

(3) The use of Geneva nomenclature to describe these compounds is cumbersome; therefore, we are following the same system used in our previous work²: that is, the simple symmetrical azines will be described as derivatives of the corresponding aldehydes or ketones, *e. g.*, benzalazine and acetophenone azine. When the azines are unsymmetrical (derived from two different aldehydes or ketones or mixed azines derived from an aldehyde and a ketone), the compound is described by naming both components with the lower molecular component named first, *e. g.*, benzaldehyde-acetophenone azine.

(4) Jones, *THIS JOURNAL*, **65**, 1818 (1943).

(5) Although the molecule may be perfectly coplanar without strain, the free rotation of the α -methyl groups is hindered, which may account for the spectral differences.

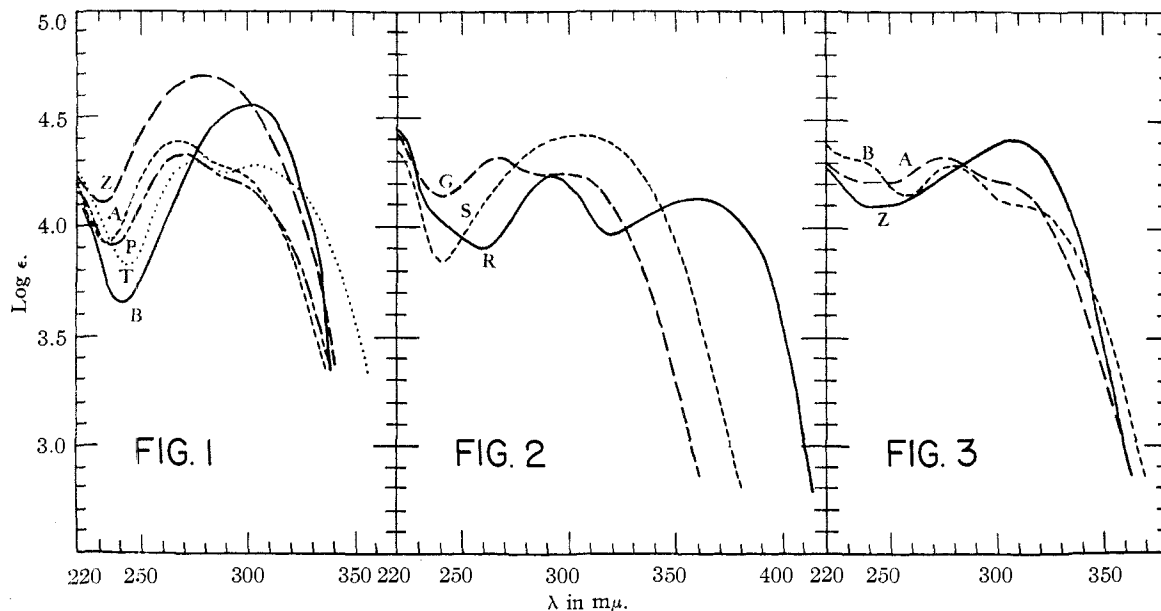
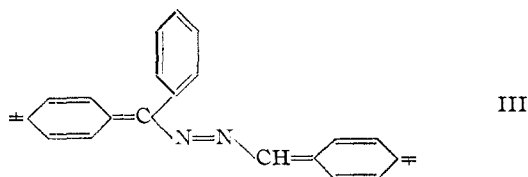


Fig. 1.—Curve B, benzalazine; Z, benzaldehyde-acetophenone azine; A, acetophenone azine; P, propiophenone azine; T, α -tetralone azine.

Fig. 2.—Curve R, 2,2'-dihydroxyacetophenone azine; G, 3,3'-dihydroxyacetophenone azine; S, 4,4'-dihydroxyacetophenone azine.

Fig. 3.—Curve Z, benzaldehyde-benzophenone azine; A, acetophenone-benzophenone azine; B, benzophenone azine.

indicates that the effective absorbing group is probably the same and may be formulated as III



where the third phenyl group lies in a plane other than that of the main absorbing unit. When, however, the second α -carbon atom is substituted by either an alkyl or an aromatic group as in the mixed azine from benzophenone and acetophenone, and benzophenone azine, respectively, the effect is to shift the main absorption maximum to shorter wave lengths but to leave an incipient maximum or inflection point at the original position. This is probably indicative of the presence of at least two absorbing systems in the molecule analogous to those described above for the α -alkyl substituted azines. To the linear coplanar form may be attributed the absorption at $305 \pm 5 \text{ m}\mu$, whereas the absorption at shorter wave lengths may be correlated with a non-planar configuration, probably associated with an absorbing unit such as II. It should be pointed out that the effect of a single α -alkyl substituent in the benzalazine series is to shift the absorption maximum approximately $28 \pm 5 \text{ m}\mu$ toward shorter wave lengths irrespective of whether there is an aromatic α -substituent in the azine molecule or not. On the other hand, alkyl or

aryl substituents in both α and α' positions of the molecule have about the same effect; that is, a shift of $28 \pm 5 \text{ m}\mu$ toward shorter wave lengths as compared with the parent compound.

The general effect of electron donating substituents upon the absorption spectra of aromatic ketazines may be observed upon consideration of the spectra shown in Fig. 4. A rather strongly electron donating group, such as the ethoxy group, when in the para position, as in 4,4'-diethoxyacetophenone azine, tends to increase the electron density in the absorbing unit in a molecule, and hence shifts the absorption maximum toward longer wave lengths as compared with the unsubstituted compound (*cf.* Fig. 1, Fig. 4). When a very strongly electron donating group such as the amino group is in the para position the effect is enhanced, and the point of maximum absorption is shifted still further toward longer wave lengths. In this case, 4,4'-diaminoacetophenone azine absorbs $66 \text{ m}\mu$ further toward the visible as compared with acetophenone azine. Thus, it is apparent that absorption at longer wave lengths depends, in a large part, on the electron density in the absorbing system as well as its length.

The spectra of the naphthalene analogs of the benzene derivatives allow for similar analysis. For example, 1,1'-naphthalazine, absorbing at $35 \pm \text{m}\mu$, absorbs at considerably longer wave lengths than its α, α' -dimethyl derivative, 1,1'-acetone naphthalene azine (Fig. 5). It should be pointed out that the latter compound does not

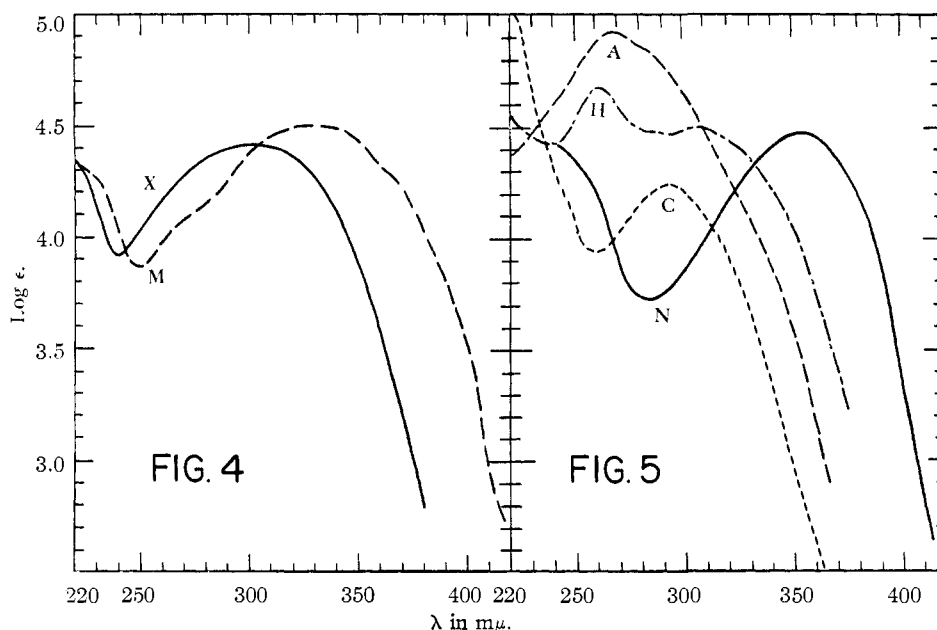
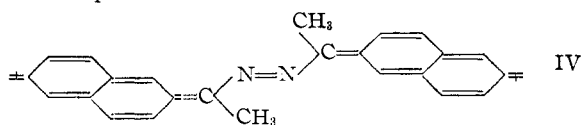


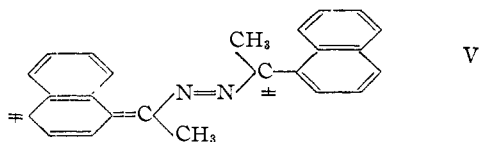
Fig. 4.—Curve X, 4,4'-diethoxyacetophenone azine; M, 4,4'-diaminoacetophenone azine.

Fig. 5.—Curve N, 1,1'-naphthalazine; C, 1,1'-acetonaphthone azine; H, 2,2'-acetonaphthone azine; A, acetophenone-2-acetonaphthone azine.

exhibit the double peaks characteristic of ketazines, and that the molecule *cannot* be coplanar without the introduction of considerable strain. The spectrum thus shows only one maximum, since coplanar forms (corresponding to I) cannot be attained. On the other hand, 2,2'-acetonaphthalene azine which can have practically the same steric configurations as acetophenone azine shows the same type of spectrum; that is, a long wave length absorption maximum at 305 $m\mu$ and a shorter wave length absorption peak in the neighborhood of 270 $m\mu$. Mention should be made that the 2,2'-substituted compound should and does absorb at slightly longer wave lengths than the azine derived for 1-acetonaphthone. This longer wave length absorption is explicable by the contribution of forms such as IV for 2,2'-acetonaphthone azine



compared with the shorter absorbing system present in forms such as V



which contribute to the spectrum of 1,1'-acetonaphthone azine. Acetophenone-2-acetonaphthone azine shows a similar although more intense

absorption than does acetophenone azine. In general, the spectra of the naphthalene azines parallel those of the benzene azines; that is, the aldazines absorb at longer wave lengths than the corresponding ketazines, which in turn show two peaks (or one peak and an inflection point) if strain-free coplanar structures can exist.

Acknowledgment.—Our sincere appreciation is expressed to Mr. Claude Valle for his valuable preparative assistance and to Misses Adelaide Sutton, Esther Polson, and Mr. W. A. Davis for the measurement of the absorption spectra.

Experimental

Preparation of Symmetrical Aromatic Ketazines.—Unlike the preparation of aldazines,² ketazines frequently require boiling at elevated temperatures for several hours to complete the reaction between the ketones and hydrazine. The preferred method involves heating an ethanol solution of the ketone with 0.45 molar equivalent of 85% hydrazine hydrate and a few drops of acetic acid for two to six hours. Generally the azine separates out on cooling but in some cases (*e. g.*, benzophenone azine) it is necessary to use a bomb tube reaction at 150–160° for the reaction to proceed beyond the hydrazone stage to the formation of the azine. The solvents used for the crystallization of the compounds described in this paper are given in Table I.

Preparation of Unsymmetrical Aromatic Azines.—In general, these compounds were synthesized by a two-step reaction involving the preparation of the hydrazone of the least reactive component, which was then reacted with the appropriate ketone or aldehyde in a manner similar to that described above.

The new compounds prepared during the course of this work are described in Table II.

The absorption spectra measurements were made on a Beckmann quartz spectrophotometer model DU using a 1-cm. quartz cell and a hydrogen discharge tube as an ultraviolet source. Absolute ethyl alcohol was used as a solvent throughout.

TABLE I

Azine	M. p., °C. reported	Observed m. p., °C. (cor.)	Crystn. solvent	Fig.	λ max. m μ	Log ϵ
Benzal	93 ^a	92.5-93	Pyridine	1	300	4.56
Benzaldehyde-acetophenone	59 ^b	58-59	Ethanol	1	278	4.68
Acetophenone	121 ^c	121-122	Ethanol	1	267	4.39
					~295	4.25
Propiophenone	79-80 ^d	64.5-65.2 ^e	Ethanol	1	270	4.32
					~295	4.22
α -Tetralone		143-144 ^e	Diox.-EtOH	1	275	4.29
					305	4.28
2,2'-Dihydroxyacetophenone		198-199 ^e	Aq. EtOH	2	293	4.24
					362	4.13
3,3'-Dihydroxyacetophenone		180-180.5 ^e	Aq. EtOH	2	268	4.32
					~297	4.25
4,4'-Dihydroxyacetophenone		222-223 ^e	Aq. EtOH	2	303	4.42
Benzaldehyde-benzophenone	75 ^f	69-70	Aq. EtOH	3	307	4.42
Acetophenone-benzophenone	105 ^f	103.5-104.5	Aq. EtOH	3	273	4.32
					~305	4.21
Benzophenone	164 ^f	164-165	Ether	3	278	4.29
					~310	4.11
4,4'-Diethoxyacetophenone		182-183 ^e	Dioxane	4	303	4.42
4,4'-Diaminoacetophenone	166 ^g	166	Ethanol	4	333	4.51
1,1'-Naphthal	156 ^h	156-157	Ethanol	5	354	4.48
1,1'-Acetonaphthone		121.5-122 ^e	Ethanol	5	293	4.25
2,2'-Acetonaphthone		212-213 ^e	Dioxane	5	262	4.68
					305	4.51
Acetophenone-2-acetonaphthone		138-139 ^e	Acetone	5	268	4.92

^a Curtius and Jay, *J. prakt. Chem.*, [2] **39**, 27 (1889). ^b Curtius and Pflug, *ibid.*, [2] **44**, 535 (1891). ^c Curtius and Thun, *ibid.*, [2] **44**, 161 (1891). ^d Knopfer, *Monatsh.*, **32**, 762 (1911). ^e See experimental section. ^f Curtius and Rauterberg, *J. prakt. Chem.*, [2] **44**, 192 (1891). ^g Knopfer, *Monatsh.*, **30**, 37 (1909). ^h Curtius, *J. prakt. Chem.*, [2] **85**, 393 (1912). ~ indicates an inflection point.

TABLE II

Azine	M. p., °C. (cor.)	Formula	Analyses, %			
			Carbon		Hydrogen	
			Calcd.	Found	Calcd.	Found
Propiophenone	64.5-65.2 ^b	C ₁₃ H ₂₀ N ₂	81.78	81.89	7.63	7.49
α -Tetralone	143-144	C ₂₀ H ₂₀ N ₂	83.29	83.55	6.99	6.69
2,2'-Dihydroxyacetophenone	198-199	C ₁₆ H ₁₆ O ₂ N ₂	71.62	71.67	6.01	6.27
3,3'-Dihydroxyacetophenone ^e	180-180.5	C ₁₆ H ₁₆ O ₂ N ₂	71.62	71.81	6.01	6.15
4,4'-Dihydroxyacetophenone ^d	222-223	C ₁₆ H ₁₆ O ₂ N ₂	71.62	71.65	6.01	6.26
4,4'-Diethoxyacetophenone	182-183	C ₂₀ H ₂₄ O ₂ N ₂	74.05	73.69	7.44	7.29
1,1'-Acetonaphthone ^e	121.5-122	C ₂₄ H ₂₀ N ₂	85.65	85.35	5.99	6.09
2,2'-Acetonaphthone	212-213	C ₂₄ H ₂₀ N ₂	85.65	85.41	5.99	6.27
Acetophenone-2-acetonaphthone	138-139	C ₂₀ H ₁₈ N ₂	83.87	83.56	6.36	6.48

^a Analyses by Dr. Carl Tiedcke. ^b This compound is described by Knopfer, *Monatsh.*, **32**, 762 (1911), as melting at 79-80°. Two different samples prepared by us melted at 64.5-65.2°. ^c *m*-Hydroxyacetophenone was prepared by the diazotization of the corresponding amino compound. ^d *p*-Hydroxyacetophenone was prepared by the Fries rearrangement of phenyl acetate according to the general method of Farinholt, Harden and Twiss, *THIS JOURNAL*, **55**, 3383 (1933). ^e The 1-acetonaphthalene was purified through its picrate before use.

Summary

The ultraviolet absorption spectra of several aromatic ketazines have been determined, and a correlation has been made between their spectra and structure. It has been shown that the replacement of the α -hydrogen of a symmetrical aromatic aldazine by an alkyl group shifts the absorption maximum at least 23 m μ toward shorter wave lengths.

This effect is not noted upon the introduction of a single aromatic substituent, but *two* aromatic or aliphatic substituents in the α and α' positions produce similar displacements toward shorter wave lengths. Further confirmation is offered that absorption depends on the electron density in an absorbing system as well as its length.

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