[CONTRIBUTION FROM THE CANCER RESEARCH LABORATORY, UNIVERSITY OF FLORIDA]

Physical Properties of Aminoazobenzene Dyes. V. The C_ϵ/A_ϵ Ratio[1]

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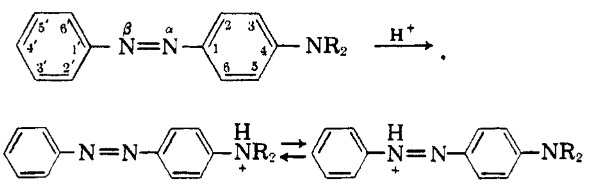
The tautomerism of 73 azobenzene derivatives in 50% ethanolic acid solution has been investigated. The reproducible, simply-obtained $C\epsilon/A\epsilon$ ratio gives a crude idea of the ratio of C (proton goes to β-nitrogen) to A (proton goes to amino nitrogen) tautomers present in acid solution. This $C\epsilon/A\epsilon$ ratio should prove to be very useful in the determination of structures of unknown azo dyes. The $C\epsilon/A\epsilon$ ratio has been correlated with basicity, resonance, inductive, steric and intra- and intermolecular hydrogen bonding effects. Approximately 100 spectra (310–600 mμ) in 50% alcoholic acid solution have been reported.

It has been shown that the 4-aminoazobenzene dyes exist in acid solution as a *p*H-dependent equilibrium mixture of tautomeric forms in which the ammonium, A, form of the salt is associated with a band near 320 mμ and the cationic resonating form, C, is associated with the long wave length band.[3]



A C

The C_ϵ/A_ϵ ratio gives a crude idea of the tautomeric equilibrium. C_ϵ is the molar extinction coefficient at the wave length maximum of the C band; A_ϵ is the molar extinction coefficient at the wave length maximum of the A band.

In the 4-aminoazobenzene dyes there are two main basic centers—at the β-nitrogen and at the amino nitrogen. The diverse effects on, and the interplay between, these two resonance terminals determines the basicity of the molecule. Other things being equal, increasing the basicity of the β-nitrogen or decreasing the basicity of the amino nitrogen increases the value of the C_ϵ/A_ϵ ratio. For example, in the 4-*N*,*N*-dialkylaminoazobenzenes, the dimethyl compound, DAB, pK_a 2.28, has a C_ϵ/A_ϵ ratio of 3.62 while the *N*-methyl-*N*-benzyl compound, pK_a 1.6, has an increased C_ϵ/A_ϵ ratio of 4.5. The benzyl group has decreased the basicity of the amino nitrogen, thus causing an over-all decrease in the first pK_a. But this has caused the β-nitrogen to be proportionally stronger in basicity and thus a greater percentage of C tautomer is formed. In this manner the basicity of the amino nitrogen could be gradually decreased; this would cause a gradual increase in the C_ϵ/A_ϵ ratio until eventually only the C tautomer would be present in solution. On the other hand in 4-methylethylaminoazobenzene, pK_a 2.58, the C_ϵ/A_ϵ ratio drops to 1.4 because of the increase in the basicity of the amino nitrogen in relation to the β-nitrogen. In 4-diethylaminoazobenzene, pK_a 3.08, the further increase in the basicity of the amino nitrogen causes a further decrease in the C_ϵ/A_ϵ ratio to 0.5. In 3-methyl DAB, pK_a 3.48, the steric effect of the 3-methyl group causes a further increase in the basicity of the amino group and a decrease in the C_ϵ/A_ϵ ratio to 0.025. This same regular effect is seen in many of the derivatives of the 4-dialkylaminoazobenzenes (compare 2'-nitro DAB, 2'-nitro MEAB and 2'-nitro DEAB or the 3'-nitro, 4'-nitro, 4'-acetyl or 3'-methyldialkylaminoazobenzenes), Table I.

It has been shown that the 2-methyl group in 2-methyl DAB increases the electron density of the β-nitrogen,[4] thus causing an increase in the pK_a to 3.08 and an increase in the C_ϵ/A_ϵ ratio to 10.0. This same effect can be seen for eleven other 2-methyl DAB derivatives, Table I.

A 2'-methyl group decreases the basicity of the β-nitrogen; the over-all effect is a decrease in the pK_a and the C_ϵ/A_ϵ ratio of the 4-dialkylaminoazobenzene. In 2'-ethyl DAB the increased steric effect causes a further drop in the basicity and C_ϵ/A_ϵ ratio. There is a drop in basicity for 2'-chloro DAB and 2'-chloro MEAB as compared to the analogous 2'-methyl derivatives. This is not unexpected for the 2'-chloro group is more base-weakening than the 2'-methyl group.[5] In spite of this the C_ϵ/A_ϵ ratios of the 2'-chloro dyes are slightly higher than the ratios of the analogous methyl derivatives. One of the factors that probably contributes to this fairly high C_ϵ/A_ϵ ratio is the presence of weak intramolecular hydrogen bonding between the 2'-chloro and the hydrogen on the β-nitrogen of the C tautomer (*i.e.* the azonium hydrogen).

In 2'-methoxy DAB steric hindrance and the resonance interaction of the methoxy group with

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[3] E. Sawicki, *J. Org. Chem.*, **21**, 605 (1956).

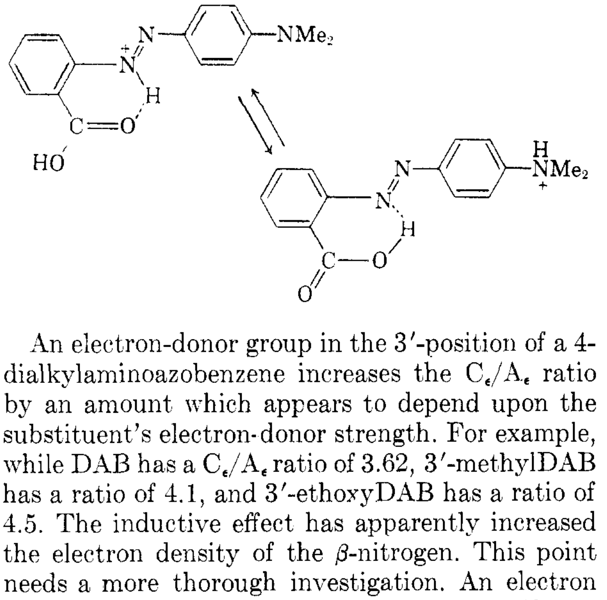
[4] E. Sawicki and F. Ray, *J. Org. Chem.*, **19**, 1686 (1954); E. Sawicki and Gerber, *J. Org. Chem.*, **21**, 410 (1956).

[5] J. Vandenbelt, C. Henrich, and S. Berg, *Anal. Chem.*, **26**, 726 (1954).

the α-nitrogen would have a base-weakening effect on the β-nitrogen. Among other effects the intramolecular hydrogen bonding involving the methoxy oxygen and the azonium hydrogen of the C tautomer would increase the proportion of that tautomer present in acid solution. Consequently it is not surprising to find a C_ϵ/A_ϵ ratio of 2.36 for this compound.

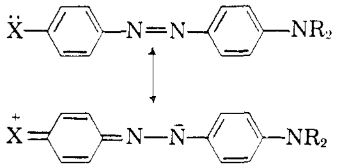
In 2′-nitroDAB the pK_a is 1.49. The powerful base-weakening inductive effect of the nitro group on the β-nitrogen and the base-weakening resonance effect on the amino nitrogen are two of the factors causing the decreased basicity. The first factor would strongly decrease the C_ϵ/A_ϵ ratio; the second factor would increase the ratio. The effect of the second factor and the formation of an intramolecular hydrogen bond between the nitro group and the azonium hydrogen would help to explain the fairly high C_ϵ/A_ϵ ratio of 1.6 for this compound.

2′-CarboxyDAB in acid solution shows a large increase in the C_ϵ/A_ϵ ratio. This can only mean that in this salt the intramolecular hydrogen bond between a carboxyl oxygen and the azonium hydrogen is strong enough to force the equilibrium C $\rightleftarrows$ A far to the left.

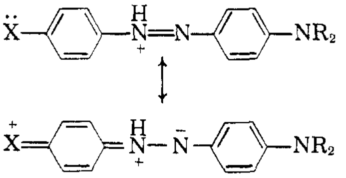


An electron-donor group in the 3′-position of a 4-dialkylaminoazobenzene increases the C_ϵ/A_ϵ ratio by an amount which appears to depend upon the substituent's electron-donor strength. For example, while DAB has a C_ϵ/A_ϵ ratio of 3.62, 3′-methylDAB has a ratio of 4.1, and 3′-ethoxyDAB has a ratio of 4.5. The inductive effect has apparently increased the electron density of the β-nitrogen. This point needs a more thorough investigation. An electron attracting group in the 3′-position has little, if any, effect on the ratio.

As the electron-donor strength of a group in the 4′-position of a 4-dialkylaminoazobenzene increases from hydrogen to methoxy, the C_ϵ/A_ϵ ratio decreases and the C band shifts toward the visible. For example, DAB has λ_{max} 516 mμ and a C_ϵ/A_ϵ ratio of 3.62; 4′-methylDAB has λ_{max} 531 mμ and a C_ϵ/A_ϵ ratio of 2.57; 4′-acetylaminoDAB has λ_{max} 545 mμ and a C_ϵ/A_ϵ ratio of 1.86; 4′-methoxyDAB has λ_{max} 548 and a C_ϵ/A_ϵ ratio of 1.00. This same order is seen in 2-methylDAB, 2,4′-dimethylDAB and 2-methyl-4′-acetylaminoDAB. The decrease in the C_ϵ/A_ϵ ratio is apparently due to the following resonance effect which would cause a slight increase in the electron density at the α-nitrogen[6] and a consequent decrease in the electron density at the β-nitrogen thus:



The shift of the C band towards the visible in these 4′-substituted derivatives is probably due to the following type of extra-conjugative resonance in the C tautomer.



The direct relation between these two resonance effects is obvious. The drop in the C_ϵ/A_ϵ ratio and the shift towards the visible on substitution of an electron-donor group in the 4′- or 2′-position[7] must be due to a resonance phenomenon for a similar substitution in the 3′-position of a 4-dialkylaminoazobenzene causes neither a strong red shift nor a decrease in the C_ϵ/A_ϵ ratio, Table I. For example, 2′-methoxyDAB, λ_{max} 540, 4′-ethoxyDAB, λ_{max} 552, and 4′-acetylaminoDAB, λ_{max} 545, show a definite red shift in dilute acid solution as compared to 3′-ethoxyDAB, λ_{max} 521, DAB, λ_{max} 516, and 3′-acetylaminoDAB, λ_{max} 518.

A 4′-halogen apparently increases the electron density of the α-nitrogen through a resonance effect. Consequently substitution of a halogen in the 4′-position of a 4-dialkylaminoazobenzene causes decreases in the C_ϵ/A_ϵ ratio and the basicity of the molecule.

As the electron-attractor strength of a group in the 4′-position of a 4-dialkylaminoazobenzene increases from hydrogen to nitro, the C_ϵ/A_ϵ ratio decreases and the long wave length zwitterionic resonance, or Z, band of the compound in alcoholic solution shifts toward the visible. For example, DAB has λ_{max} 408 mμ and a C_ϵ/A_ϵ ratio of 2.57; 4′-thiocyanoDAB[8] has λ_{max} 433 mμ and a C_ϵ/A_ϵ ratio of 4.54; 4′-acetylDAB has λ_{max} 447 mμ and a

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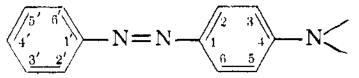
(6) For more powerful electron-donors, such as the alkylthio or amino groups the electron density at the α-nitrogen would be expected to be large enough for this nitrogen to seriously compete with the β- and amino nitrogens for the proton.

(7) However in the 2′-position steric, inductive and intramolecular hydrogen bonding effects could also be of some importance.

(8) The thiocyano group has been shown to be electron-attracting through basicity [M. Rogers, T. Campbell, and R. Maatman, *J. Am. Chem. Soc.*, **73**, 5122 (1951)] and electric moment data [T. Campbell and M. Rogers, *J. Am. Chem. Soc.*, **70**, 1029 (1948)].

TABLE I

C_ϵ/A_ϵ RATIOS OF 4-AMINOAZOBENZENE DYES



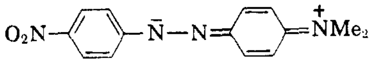
Compound	pK_a[a]	λ_{max}[b], mμ($\epsilon \times 10^{-3}$)		HCl, Normality	$\frac{C_\epsilon}{A_\epsilon}$
		C Band	A Band		
2-AB[c]	1.8	....	328[d](20.3)	1.0	0.00
4',5-diMe-2-AB	2.5	....	350[e](23.6)	1.0	0.00
3-AB	3.0	....	320[f](18.0)	1.2	0.00
4-AB	2.28	500(12.2)	318–320(16.8)	1.0	0.73
		500(16.5)	318–320(15.8)	2.0	1.0
		500–504(36.7)	318–320(9.16)	6.0	4.0
2,3'-diMe-4-AB	2.92	500(31.0)	330(10.0)	1.0	3.1
2,4'-diMe-4-AB	2.92	510(26.0)	332(12.2)	1.0	2.1
3,4'-diMe-4-AB	2.39	510(17.5)	330–332(16.9)	1.0	1.0
2',3-diMe-4-AB	2.29	488–490(2.40)	326(19.1)	1.0	0.13
MAB[g]	2.37	505(40.9)	320(7.64)	1.2	5.4
3'-MeMAB	2.43	510–512(42.6)	320–322(7.40)	1.2	5.8
EAB[h]	2.58	512–516(36.3)	318–320(9.96)	1.2	3.6
DAB[i]	2.28	514–520(34.0)	320(10.14)	0.6	3.4
		512–520(35.5)	320(9.8)	1.2	3.6
		514–518(40.3)	320(8.10)	3.0	5.0
		516–520(47.3)	322–324(5.26)	6.0	9.0
MEAB[j]	2.58	516(21.5)	318(15.2)	1.0	1.4
		516(23.6)	318(14.4)	2.0	1.6
DEAB[k]	3.08	518(9.50)	318(19.5)	1.0	0.49
		517(10.8)	318(19.2)	2.0	0.56
MBAB[l]	1.6	526(41.2)	318–324(9.20)	1.2	4.5
3-MeDAB	3.48	500[m](0.50)	319(19.8)	1.0	0.025
4'NO$_2$-3-MeDAB		490–494(1.02)	328(25.5)	3.0	0.040
		506–510(1.26)	328(25.2)	6.0	0.050
4'-Ac-3-MeDAB	3.27	484–486(0.984)	325(28.3)	0.6	0.035
		494–496(1.07)	325–327(27.9)	3.0	0.038
		510–512(1.29)	325(27.7)	6.0	0.047
3'-NO$_2$-3-MeDAB	3.18	~500[n](0.34)	310(22.4)	1.2	0.015
2-MeDAB	3.08	514(48.2)	326–328(4.82)	1.2	10.0
		514–516(49.9)	328(4.20)	3.0	11.9
		514–515(53.0)	330–334(3.14)	6.0	16.9
2,2'-DiMeDAB	2.64	510(15.3)	332(13.8)	1.0	1.1
2'-Me-2'-COOHDAB		516(52.5)	336(4.20)	3.0	12.5
2-Me-2'COOCH$_3$DAB		510–514(51.5)	336–338(4.16)	0.6	12.4
		512–514(51.8)	332–336(4.10)	1.2	12.6
		516(51.0)	336(4.00)	3.0	12.8
		514–520(53.1)	336–338(3.58)	6.0	14.8
2-Me-2'-NO$_2$DAB	2.12	502–510(40.0)	318–320(8.6)	1.2	4.7
2-Me-3'-Cl-DAB	2.67	506–508(48.1)	328–330(5.04)	1.2	9.5
2-Me-3'-AcDAB	2.73	504–508(49.4)	324(5.56)	1.2	8.9
2,4'-DiMeDAB		530(45.2)	334–336(6.60)	1.2	6.9
		530(48.0)	336–338(5.44)	3.0	8.8
2-Me·4' AcDAB	2.88	510(62.1)	320(5.68)	1.2	10.9
		514–516(63.4)	320(5.64)	3.0	11.2
2-Me-4'-NO$_2$DAB		510(56.3)	340(5.72)	1.2	9.8
		510(66.0)	340–342(5.40)	3.0	12.2
2-Me-4'-NHAcDAB		545(44.5)	352–357(8.60)	1.2	5.2
2'-MeDAB	2.04	515(5.10)	325(17.6)	1.2	0.29
2'-EtDAB	1.85	510(2.60)	332(18.1)	1.0	0.14
2'-OMeDAB	2.20	540(21.0)	320[o](8.90)	1.0	2.4
		540(25.5)	318[o](8.16)	3.0	3.1
2'-ClDAB	1.74	500(5.40)	320(17.0)	1.0	0.32
2'-NO$_2$DAB	1.5	509(19.8)	315(12.4)	1.0	1.6
2'-COOHDAB		518(43.4)	325–330(3.32)	1.2	13.1
2'-MeMEAB		505–510(2.24)	328(19.2)	1.2	0.12
2'-Cl-MEAB	2.14	500(2.50)	320–324(17.8)	1.2	0.14
2'-NO$_2$-MEAB	1.75	508(10.7)	320(15.0)	1.0	0.7
2',5'-DiMeDAB	2.0	520(5.70)	327(16.7)	1.0	0.34
2',4',6'-TriBrDAB	1.0	450(4.20)	315(10.0)	1.0	0.42
		460–465(8.10)	315(9.80)	6.0	0.83
3'-MeDAB	2.33	522–526(37.6)	320–326(9.2)	1.2	4.1
3'-EtODAB		520–522(36.6)	318(8.16)	1.2	4.5

TABLE I (*Continued*)

3′-NHAcDAB	2.27	518(36.2)	318(9.16)	1.2	4.0
3′-ClDAB	2.01	510–514(35.3)	316–318(9.96)	1.2	3.6
3′-AcDAB	2.03	509(37.3)	312–318(10.3)	1.2	3.6
3′-NO_2DAB	1.67	500(37.8)	310–312(10.52)	1.2	3.6
3′-CF_3DAB	1.84	500(34.4)	312–314(10.76)	1.2	3.2
3′-MeMEAB		518–524(23.7)	322–326(13.84)	1.2	1.7
3′-NHAcMEAB	2.47	520(22.2)	315(13.6)	1.2	1.6
3′-ClMEAB		510–512(22.2)	318(15.0)	1.0	1.5
3′-AcMEAB	2.28	510(21.2)	316(14.4)	1.0	1.5
3′-NO_2MEAB	2.0	500(23.6)	312–314(15.2)	1.2	1.6
3′-CF_3MEAB	2.15	504–506(20.5)	314(15.4)	1.2	1.3
3′-MeDEAB		520(11.16)	322–324(18.8)	1.2	0.59
3′-NO_2DEAB	2.39	502–504(10.8)	310–314(19.36)	1.2	0.56
4′-MeDAB	2.36	530–532(31.7)	330–334(12.32)	1.2	2.6
		532(45.3)	332–334(6.60)	6.1	6.9
4′-EtDAB	2.30	530–534(31.7)	332–334(12.4)	1.2	2.6
		532–534(45.7)	334(6.60)	6.1	6.9
4′-*i*-PrDAB	2.31	532–534(32.3)	330–336(12.52)	1.2	2.6
		532–534(46.0)	334–338(6.8)	6.1	6.8
4′-MeODAB	2.40	548(18.5)	352(18.2)	1.2	1.0
		550(20.0)	352(17.1)	2.0	1.2
4′-EtODAB		550–554(18.8)	354(18.8)	1.2	1.0
4′-NHAcDAB	2.25	545(28.3)	352(15.2)	1.2	1.9
4′-FDAB	2.00	517(21.4)	320(14.4)	1.0	1.5
4′-SCNDAB		516(44.3)	330(9.76)	1.2	4.5
4′-AcDAB	2.16	516–524(58.4)	$\underline{320}$(7.76)	1.2	7.5
		512–518(59.4)	$\underline{320}$(7.12)	3.0	8.3
4′-NO_2DAB	1.81	512(61.6)	332(7.10)	1.0	8.7
4′-EtMEAB	2.72	532(13.7)	333(14.4)	1.0	0.95
4′-FMEAB	2.40	519(10.8)	320(17.8)	1.0	0.61
4′-AcMEAB	2.35	515(46.3)	322(11.44)	1.2	4.0
		515–517(50.8)	$\underline{320}$(10.4)	3.0	4.4
4′-NO_2MEAB		506(67.8)	328(10.04)	1.2	6.8
4′-AcDEAB		515(29.3)	322–325(17.72)	1.2	1.7
4′-NO_2DEAB		510(40.0)	325–327(15.8)	1.2	2.5

[a] Reference 3. [b] Determined from 300 to 600 mμ in 50% alcoholic hydrochloric acid. [c] AB is aminoazobenzene. [d] Two shoulders are found at 410 and 570 mμ. In 50% alcoholic 6*N* hydrochloric acid these shoulders are intensified into bands—one at 420 mμ, ε 900, due to the R band analogous to the R band of azobenzene, the other at 570 mμ, ε 738 either due to an impurity or a slight amount of C tautomer. [e] As in 2-AB two weak bands are found at 430 and 600 mμ. [f] Band is also found at 430 mμ, ε 810 which is an R band. [g] MAB is 4-methylaminoazobenzene. [h] EAB is 4-ethylaminoazobenzene. [i] DAB is 4-dimethylaminoazobenzene. [j] MEAB is 4-methylethylaminoazobenzene. [k] DEAB is 4-diethylaminoazobenzene. [l] MBAB is 4-methylbenzylaminoazobenzene. [m] Band at 444 mμ, ε 630 is an R band. All underlined values are shoulders. [n] Determined for comparison. Band at 452 mμ, ε 550 is an R band. [o] Another A band is found at 360 mμ, ε 7200.

C_ϵ/A_ϵ ratio of 7.52; 4′-nitroDAB has λ_{max} 477 and a C_ϵ/A_ϵ ratio of 8.7. This same relation is seen for the 4′-acetyl and 4′-nitro derivatives of MEAB and DEAB. The increase in the C_ϵ/A_ϵ ratio is probably caused by an increase in the electron density of the β-nitrogen and a decrease in the basicity of the amino nitrogen. This decrease in basicity and the shift of the Z band toward the visible most likely stems from the greater contribution in the ground state (as compared to DAB) of the zwitterionic resonance structure



Comparison of the C_ϵ/A_ϵ ratios of 4-amino-, 4-alkylamino- and 4-dialkylamino-azobenzenes discloses that the C_ϵ/A_ϵ ratios decrease in the order $-NHR > NR_2 > NH_2$. Apparently at least two opposing factors are at work. The alkyl groups would tend to increase the electron density of the amino nitrogen through an inductive effect and would tend to decrease the electron density of the amino nitrogen because of the decrease in solvation energy stabilization since the alkyl groups do not form hydrogen bonds with the solvent molecules.[9]

Isomeric alkyl derivatives are usually difficult to differentiate, but by use of the C_ϵ/A_ϵ ratio the five monomethyl-DAB isomers can be readily distinguished, Table I.

EXPERIMENTAL

Preparations. All the dyes were available from other investigations in this laboratory and had been purified by numerous crystallizations from two to five different solvents.[4] Chromatography was used where necessary.

Absorption spectral data. The spectra of all compounds were measured with a Beckman Model DU Spectrophotometer from 300 to 600 mμ in 50% alcoholic 1.2*N* hydrochloric acid solution, unless otherwise stated. This solution consisted of 50 ml. of 2.4*N* aqueous hydrochloric acid (200 ml. of concentrated hydrochloric acid diluted to 1000 ml. with distilled water) and the necessary volume of a 95% alcoholic solution of the azo dye, diluted to 100 ml. with commercial 95% ethanol.

Most of the C_ϵ/A_ϵ ratio values have been obtained at a

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(9) A. Trotman-Dickenson, *J. Chem. Soc.*, 1293 (1949).

hydrochloric acid normality of 1.0 or 1.2. At this normality the vast majority of the 4-aminoazobenzene dyes show slight changes in the C_ϵ/A_ϵ ratio with a change in normality. For more basic compounds (such as 4′-amino DAB) this ideal plateau would be found at a lower normality. The ideal situation would be to obtain C_ϵ/A_ϵ values at the lowest normality at which a 100% of the monocationic salt was present. It is felt that the determination of the C_ϵ/A_ϵ ratio at a normality of 1.0 to 1.2 in most cases is close to the ideal situation and, although less accurate, is a much simpler procedure. Consequently it would be of greater value for the determination of the structure of an unknown azo dye.

GAINESVILLE, FLA.

[CONTRIBUTION FROM THE CANCER RESEARCH LABORATORY, UNIVERSITY OF FLORIDA]

Ultraviolet-Visible Absorption Spectra of Quinoxaline Derivatives[1]

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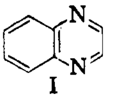
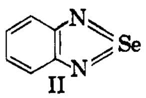
Over forty ultraviolet-visible absorption spectra of fifteen quinoxaline derivatives have been determined in alcoholic and acidic solutions. The spectra and the structure of the cations are discussed. Several new quinoxaline derivatives have been prepared.

In a previous paper[3] a number of 2,1,3-benzoselenadiazoles or piaselenoles, were prepared as possible purine antagonists. The spectra of the piaselenole derivatives were also investigated in the hope of shedding more light on the spectral properties of biologically important heterocyclic ring systems. For this reason it was decided to investigate the spectral properties of the quinoxalines, which are potential folic acid antagonists.

If one considers the tetravalent organoselenium atom, =Se=, as being somewhat similar to the =CH—CH= group, then a striking resemblance is evident between quinoxaline, I, and the tetravalent selenium structure of piaselenole, II. Like the piaselenoles, quinoxaline derivatives form monocationic and dicationic salts. The dicationic salts usually absorb at the longest wave length and the bases at the shortest wave length.


I



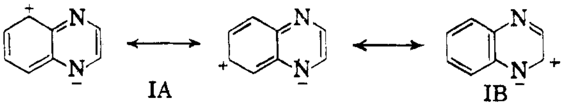
II

In 2,3-dimethyl- or 2,3-diphenyl-quinoxaline subsitution of an electron-donor group in the 6-position causes an increasing bathochromic shift in the order H < OCH_3 < C_6H_5 < SCH_3 < NH_2 for the base and monocationic forms and, except for the more strongly basic amino compound, for the dicationic compounds, Table I. The same order has been found for the analogously substituted 2,1,3-benzoselenadiazole derivatives[3] and in *para* substituted triphenylmethane dyes.[9] The fused benzene ring in 2,3-diphenyl-1,4-diazaanthracene is approximately equivalent in electron-donor properties to the 6-methoxy group as shown by the spectral data, Table I.

The sequence of proton addition in the 6-substituted quinoxalines (in the absence of an amino group) is shown in the spectra of 6-methylthio-2,3-diphenylquinoxaline, Fig. 1. In the important zwitterionic resonance structures of this compound, the 4-nitrogen is the electron-attracting resonance terminal and consequently has the greatest electron density and thus attracts the first proton.

In 2,3-symmetrically disubstituted quinoxalines the bathochromic shift increases in the series H < CH_3 < C_6H_5 < $C_6H_4OCH_3$ < $C_6H_3O_2CH_2$ < $CH = CH - C_6H_5$ < $(CH = CH)_2C_6H_5$[10] < $(CH = CH)_3C_6H_5$.[10]

Some of the zwitterionic resonance forms which are strong contributors to the excited state are


IA IB

Thus substitution of an electron-donor group in the 2,3,5,6,7 or 8 positions should cause the excited state structure to be of lower energy than IA or IB because the substituent(s) would accept the positive charge much more readily than would the unsubstituted position and consequently the compound(s) would absorb at longer wavelength.

The quinoxaline derivatives formed monocationic salts in 50% alcoholic 6*N* hydrochloric acid with the exception of the amino derivatives which

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[3] E. Sawicki and A. Carr, *J. Org. Chem.*, **22**, 503 (1957).

[4] R. Bost and E. Towell, *J. Am. Chem. Soc.*, **70**, 903 (1948).

[5] H. Goldstein and M. Streuli, *Helv. Chim. Acta*, **20**, 650 (1937).

[6] F. Bell and J. Kenyon, *J. Chem. Soc.*, 2708 (1926).

[7] H. Gilman and H. Broadbent, *J. Am. Chem. Soc.*, **70**, 2619 (1948).

[8] G. Bennett and G. Willis, *J. Chem. Soc.*, 1960 (1928).

[9] N. Deno, J. Jaruzelski, and A. Schriesheim, *J. Org. Chem.*, **19**, 155 (1954).

[10] F. Bohlmann, *Chem. Ber.*, **84**, 860 (1951).