Pakistan J. Sci. Ind. Res., Vol. 13, No. 3, October 1970

STUDIES ON HETEROCYCLICS

Part I.—The Ultraviolet Spectra of Some Quinoxaline Derivatives

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(Received August 6, 1969; revised October 10, 1969)

The UV spectra of a number of quinoxaline-3-ones, their *N*-methyl analogues and *N*-oxides are determined in ethanol and in ethanolic sulphuric acid, and their spectral characteristics are discussed.

The availability of a number of quinoxaline-3-ones and their *N*-oxides in these laboratories through the base-catalysed intramolecular cyclisation of appropriate α-substituted *o*-nitroacetanilides to corresponding 2-substituted quinoxaline-3-one-1-oxides[1,2] prompted us to investigate their spectroscopic characteristics. The results of UV spectra are being presented in this publication.

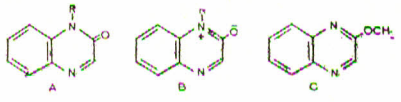
The spectra of aromatic hydrocarbons show a close resemblance to their aromatic aza analogues, and the bands due to π–π transitions can easily be distinguished in both the systems. However, monocyclic aza hydrocarbons show, apart from bands due to π–π transitions, bands at longer wavelength due to n–π transitions. These bands arise due to the excitation of an electron from the nonbonding orbital at the nitrogen to an unoccupied π orbital.[3,4] In polar solvents the n–π bands are shifted to shorter wavelengths and in some cases they may well be hidden under the π–π bands. Thus, the spectrum of pyridine shows a band due to n–π transition as a shoulder on the π–π bands. In the case of monocyclic diazines a well-defined band at longer wavelength can easily be recognised. Quinoxaline in ethanol shows more intense π–π bands than napthalene and in addition there is a shoulder at the longer wavelength due to n–π absorption.[5]

Experimental

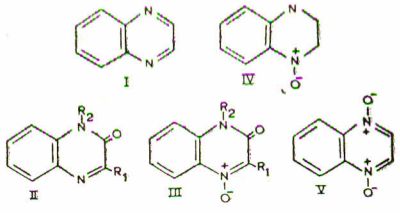
The preparations of 2-substituted quinoxaline-3-ones and the corresponding 1-oxides are reported in references 1 and 2. Quinoxaline-1-oxide, quinoxaline-3-one-1-oxide and quinoxaline-1,4-dioxide were prepared by methods reported in references 11 and 12. The UV spectra were determined with a Beckmann DK2 spectrophotometer as solutions in 95% ethanol. The spectra of protonated species were determined in 0.1N ethanolic sulphuric acid.

Discussion

Cheeseman,[6] determined the spectra of some quinoxaline-2- and -3-ones and found that the spectrum of neutral molecule of quinoxaline-3-ones was similar to that of its *N*-methyl analogue but dissimilar from that of 3-methoxy derivative; indicating that they existed predominantly in the keto form. Additionally, in solution 2-aminoquinoxaline existed predominently in the amino form and 2-mercaptoquinoxaline in the thioamide form. The cations of 2-hydroxyquinoxaline and its *N*-methyl derivative also showed similar spectra since the neutral molecules are stabilised by structures such as B, such stability is not possible in the corresponding 2-methoxy derivative C.



The absorption maxima and extinction coefficient of quinoxaline (I), 2-substituted quinoxaline-3-ones and their *N*-methyl analogues (IIa–IIg), 2-substituted quinoxaline-3-one 1-oxides (IIIa–IIId), quinoxaline-1-oxide (IV) and quinoxaline-1,4-dioxide (V) in ethanol and in 0.1N ethanolic sulphuric acid are shown in Table 1. (see Figs. 1,2 and 3).



a, $R_1=R_2=H$
b, $R_1=CH_3$; $R_2=H$
c, $R_1=R_2=CH_3$
d, $R_1=Ph$; $R_2=H$
e, $R_1=Ph$; $R_2=CH_3$
f, $R_1=COOEt$; $R_2=H$; (7 chloro-)
g, $R_1=COOEt$; $R_2=CH_3$; (7 chloro-)

a, $R_1=R_2=H$
b, $R_1=Ph$; $R_2=H$
c, $R_1=Ph$; $R_2=CH_3$
d, $R_1=CN$; $R_2=H$

TABLE 1.—ABSORPTION MAXIMA λ_{max} (mμ) AND EXTINCTION COEFFICIENTS (log ε) OF QUINOXALINE DERIVATIVES IN ETHANOL AND IN 0.1N ETHANOLIC SULPHURIC ACID.

Compound	Absorption maxima (λ_{max}) (mμ)	Extinction coefficient (log ε)
I*	233,315	4.40,3.78
IIa†	287,343	3.70,3.74
IIb	276,330	3.64,3.72
IIc	276,330	3.69,3.76
IId	304,355	4.16,4.19
IIe	304,355	3.90,3.91
IIf	294,350	3.83,3.84
IIg	292,350	3.80,3.88
IIIa	296,340 (357)	3.93, 3.68 (3.59)
Protonated	295,341 (358)	3.98,3.72 (3.60)
IIIb	(322),352	3.94,3.97
Protonated	316,351	3.60,3.69
IIIc	(322) 351	4.08,4.09
Protonated	316,352	4.00,4.11
IIId	(306),317,392	4.05,4.03,3.79
Protonated	(307),318,392	4.05,4.06,3.82
IV	315,(335)	4.00,3.89
Protonated	318, (340)	3.92, 3.83
V	313,337,373	3.78,3.80,3.78
Protonated	289,373	3.47,403.

*Values from reference 9. †Values from reference 6 (in water). The values in parenthesis ( ) indicate inflections.

The similarity in the UV spectra of 2-methyl- and 2-phenyl quinoxaline-3-ones (IIb and IId) and their corresponding *N*-methyl anaogues (IIc and IIe) indicate that they exist in solution predominantly in the keto form. However, the discovery that 3-hydroxypyroles substituted in the 2-position with a carbonyl group exist usually as hydroxy tautomers[7] led us to examine the spectra of 7-chloro-2-carbethoxyquinoxaline 3-one and its *N*-methyl analogue (IIf and IIg). In the case of 2-ethoxycarbonyl-3-hydroxypyroles the intramolecular hydrogen bonding between the carbonyl and adjacent hydroxy group leads to the stabilization of the hydroxy tautomer. The spectra of 7-chloro-2-ethoxycarbonylquinoxaline-3-one (IIf) and its *N*-methyl analogue (IIg) were similar and it appears that even the presence of the adjacent carbonyl group in quinoxaline-3-ones does not lead to significant stabilization of the hydroxy tautomer.

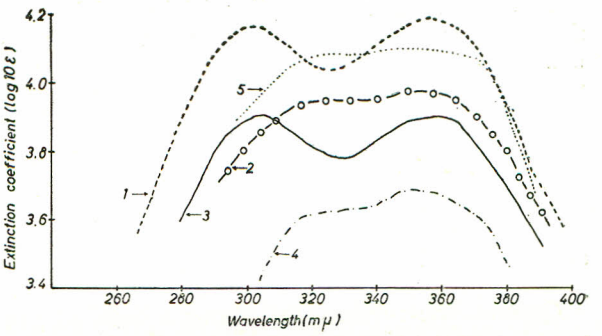


Fig. 1—*1.* 2-Phenylquinoxaline-3-one (IId);
2. 2-Phenylquinoxaline-3-one 1-oxide (IIIb;
3. 4-Methyl 2-Phenylquinoxaline-3-one (IIe);
4. 2-Phenylquinoxaline-3-one 1-oxid (IIIb protonated);
5. 4-Methyl 2-Phenylquinoxaline-3-one 1-oxide (IIIc).

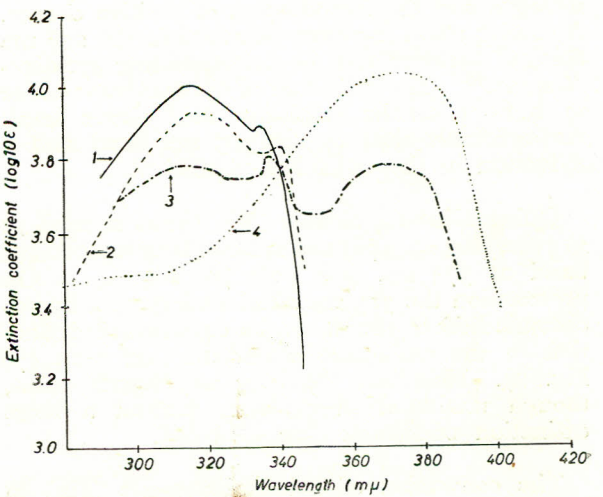


Fig. 2.—*1.* Quinoxaline-1-oxide (IV);
2. Quinoxaline-1-oxide (Protonated) (IV);
3. Quinoxaline-1,4-dioxide (V);
4. Quinoxaline-1,4-dioxide (Protonated).

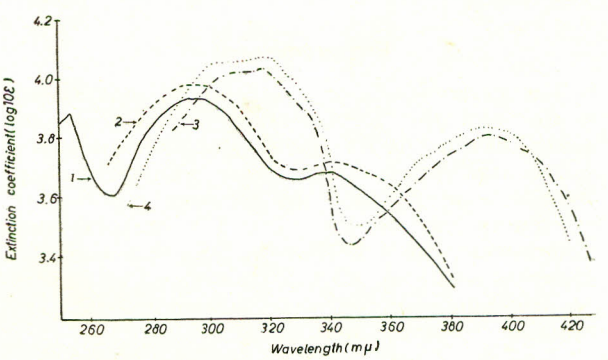


Fig. 3.—1. Quinoxaline-3-one 1-oxide (IIIa);
2. Quinoxaline-3-one 1-oxide (protonated);
3. 2-Cyano Quinoxaline-3-one 1-oxide (IIId);
4. 2-Cyano Quinoxaline-3-one 1-oxide (protonated).

The spectrum of quinoxaline (I) in cyclohexane shows bands at 316, 280 and 232 mμ attributed to π–π transitions and a band at 339 mμ to n–π transition.[8a,b] In polar solvents, e.g. methanol, two bands at 233 and 315 mμ can be recognised,[9] the less intense band shifts to lower wavelengths where it is obscured by π–π bands. Conversion of quinoxaline to quinoxaline-3-one (IIa) results in a bathochromic shifts of both the bands which are now found at 282 and 346 mμ.

Quinoxaline-1-oxide (IV) shows a band at 315 mμ (log ε=4.00) together with an inflection at 335 mμ. A similar band was found in quinoxaline but of a low extinction coefficient (ε=3.78). The increase in the extinction coefficient of the 315 mμ band in quinoxaline-1-oxide can be attributed to the tying up of the lone pair of electrons at the nitrogen and the introduction of positive charge. A similar effect has been observed in the 256 mμ band of pyridine and the corresponding pyridine-*N*-oxide.[10] The spectrum of quinoxaline-1-oxide in 0.1N ethanolic sulphuric acid shows small bathochromic shift in the 315 mμ band and a reduction in the extinction coefficient.

Quinoxaline-1,4-dioxide (V) shows a band at 313 mμ, (log ε=3.78) and another long wavelength band at 373 mμ (log ε=3.78; Fig. 2). On protonation the 313 mμ band undergoes a hypsochromic shift to 289 mμ and a considerable reduction in the extinction coefficient (log ε=3.47; Fig. 2). However, the long wavelength band, though unaltered in position, showed a large extinction coefficient (log ε=4.03).

The conversion of quinoxaline-3-one (IIa) to quinoxaline 3-one-1-oxide (IIIa) results into the bathochromic shift of both the bands and a slight increase in the extinction coefficients (Table 1). The UV spectra of 2-phenyl quinoxaline-3-one-1-oxide and its *N*-methyl derivative (IIIb, IIIc) and those of their protonated species were similar indicating that they too exist in solution in the keto form. Substitution of quinoxaline-3-one-1-oxides in 2-position with phenyl and cyano groups results into the pronounced shifts of longer wavelength bands in accordance with the substituent effects.

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