

STUDIES ON HETEROCYCLICS

Part III. The IR Spectra of Some Quinoxaline N-oxides

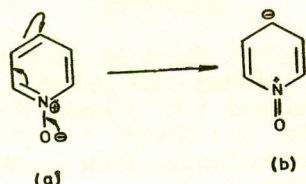
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(Received April 11, 1972; revised July 29, 1972)

Abstract. The IR spectra of several quinoxaline 1-oxides, quinoxaline 1,4-dioxides, quinoxalin-3-one 1-oxides and 1-hydroxyquinoxalin-2,3-diones (2,3-dihydroxyquinoxaline 1-oxides) have been determined. Assignments for ring stretching vibrations, carbonyl stretching frequencies and N-oxide vibrations have been suggested.

Considerable work has been reported on the IR spectra of aliphatic and aromatic N-oxides. While aliphatic N-oxides exhibit intense N⁺—O⁻ stretching vibrations¹ in the region 970–950 cm⁻¹, aromatic N-oxides show strong N—O stretching vibrations²⁻⁴ between 1300 cm⁻¹ and 1200 cm⁻¹. This higher value is explained, in pyridine N-oxides for instance, by the contribution of structure b



No systematic information on the IR spectra of quinoxaline N-oxides is, however, available and such a study was therefore considered appropriate.

In continuation of our studies⁵ on the spectral characteristics of quinoxaline derivatives, we have examined the IR spectra of some quinoxaline N-oxides. Several workers have described the IR spectra of quinoxaline derivatives.^{3,4,6,10} Clemo and Daglish¹¹ have reported the N-oxide band in quinoxaline 1-oxide at 1370 cm⁻¹ and a weaker band at 1100 cm⁻¹. Quinoxaline 1,4-dioxide also exhibits N—O stretching vibrations at 1370 cm⁻¹.

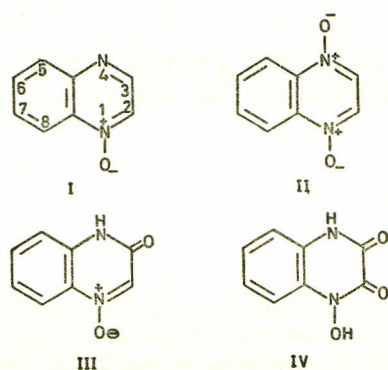
Several quinoxaline 1-oxides, quinoxaline-1,4-dioxides, quinoxalin-3-one 1-oxides and 1-hydroxyquinoxalin-2,3-diones (2,3-dihydroxyquinoxaline 1-oxides) have already been reported¹³ and the others were prepared by the methods cited in the literature.^{13,14} The IR spectra of these compounds were measured as KBr discs and the bands observed are tabulated in Table 1.

By analogy with the assignments made by Rydon and Undheim⁸ in their study of quinoxalines, the bands observed in the 1625–1440 cm⁻¹ region of the

TABLE 1. CHARACTERISTIC BAND* (cm⁻¹) IN THE IR SPECTRA OF SOME QUINOXALINE 1-OXIDE AND QUINOXALINE 1,4-DIOXIDES.

	N—OH stretching vibrations	C—O stretching vibrations	C—C & C—N ring stretching vibrations	N ⁺ —O ⁻ stretching vibrations	Other bands
<i>Quinoxaline 1-oxides</i>					
Unsubstituted	—	—	1575s, 1504s, 1429w	1379m	889s (2H), † 810m, 758s
2-Phenyl	—	—	1563w, 1493w, 1453w	1355s	889s (1H)†, 817s, 780s, 766s
2,3-Diphenyl	—	—	1575w, 1481m, 1449w	1350s	984s**, 794w, 759s
<i>Quinoxaline 1,4-dioxides</i>					
Unsubstituted	—	—	1481w	1342s	909s, 760s (4H)†, 704s
2-Phenyl	—	—	1493w	1370s	870s (1H)†, 837s, 769m, 755m, 738s (4H)†
2,3-Biphenyl	—	—	1575w, 1480m, 1450s	1333s	930m, 900s, 772w, 760m, 705m
2,3-Dimethyl	—	—	1630m 1505m	1370w	820m, 784s
6-Methyl	—	—	1527m 1460m	1364s	885w, 844w, 816s (2H)†, 797s
<i>Quinoxalin-3-one 1-oxide</i>					
Unsubstituted	—	1667s	1615m, 1540m, 1499m, 1460m	1395m	862w, 844m, 763s (4H)†
2-Cyano-7-methoxy	—	1675s	1616w, 1545m, 1493w, 1460w	1397m	826m, 746w, 702m
2-Cyano-7-ethoxy	—	1675s	1600w, 1527m, 1490m, 1460w	1399s	870m (1H)†, 815m, 800w, 746m
2-Cyano-7-chloro	—	1670s	1625w, 1535m, 1500w	1400s	877w(2H)†, 755m, 733w
<i>1-Hydroxy quinoxalin-2,3-diones</i> (2,3-dihydroxyquinoxaline 1-oxides)					
Unsubstituted	3325w	1635s, 1690-1730s	1628m, 1512 w	—	878m (4H)†, 754s, 722s
7-Methoxy	3350s	1635-1675s	1504m	—	937m, 858s, 805w, 735s
7-Ethoxy	3450m	1670-1725s	1626m, 1504w	—	845m, 797s, 738s
7-Chloro	3400s	1670-1725s	1613m, 1493m	—	866m, 810m, 763m, 714w

* s, strong; m, medium; w, weak. †, out-of-plan bending of aromatic hydrogens. **, in-plan bending.



spectra of quinoxaline 1-oxides and 1,4-dioxides were assigned to in-plane aromatic ring vibrations. The *N*-oxide band in quinoxaline 1-oxide occurred at 1379 cm^{-1} , which is close to that reported by Clemo and Daglish.¹¹ However, in 2-phenylquinoxaline 1-oxide and 2,3-diphenylquinoxaline 1-oxide, the *N*-O stretching vibrations occurred at 1355 cm^{-1} and 1350 cm^{-1} respectively, illustrating the sensitivity of *N*-O stretching vibrations to substituents effects.

Quinoxaline 1,4-dioxides exhibited weak ring stretching vibrations and stronger *N*-O bands. In 2,3-dimethylquinoxaline 1,4-dioxide, the ring stretching vibrations of medium intensity occurred at 1603 cm^{-1} and 1505 cm^{-1} . The more intense *N*-oxide band occurred at 1370 cm^{-1} . Strong *N*-oxide bands were observed in 2-phenylquinoxaline-1,4-dioxide and 6-methylquinoxaline-1,4-dioxide at 1370 cm^{-1} and 1364 cm^{-1} respectively.

Quinoxalin-3-one 1-oxides showed characteristic *C*=O stretching vibrations between 1600 – 1700 cm^{-1} . Fairly intense *N*-oxide bands were observed around 1397 cm^{-1} . The 1-hydroxyquinoxalin-2,3-diones (\equiv 2,3-dihydroxyquinoxaline 1-oxides) exhibit broad

C=O stretching vibrations in the region 1635 to 1725 cm^{-1} , weak ring stretching vibrations at about 1390 cm^{-1} and strong *N*-OH bands at 3325 – 3450 cm^{-1} .

The assignment of *N*-O stretching vibrations in some of the quinoxaline derivatives was complicated by the presence of strong ring stretching vibrations in the same region.

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