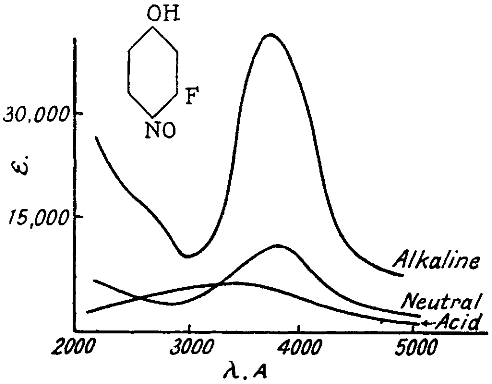
32. *The Tautomerism of Benzoquinone*-p-*Nitrosophenol Systems. Part II.* 3-*Fluoro*-4-*nitrosophenol.*

By Herbert H. Hodgson.

Previous work on the ultra-violet absorption spectra of the 3-halogeno-4-nitrosophenols and their isomeric oximes is now completed by the study of the absorption spectrum of 3-fluoro-4-nitrosophenol. This spectrum has unique features in accord with the experimental observation that this phenol, unlike its analogues, is not directly convertible into a quinonoid isomeride.

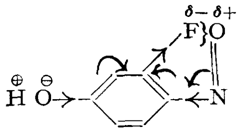
A study of the ultra-violet absorption spectra of 3-chloro-, 3-bromo-, and 3-iodo-4-nitrosophenols had indicated (Hodgson, J., 1937, 520) that in neutral alcoholic solution there were two bands with peaks at *ca.* 4000 and 3000 A., corresponding respectively to the ion and the un-ionised compound. The former band was eliminated by acids, and the latter by alkalis. Similar bands with peaks at *ca.* 4000 and 3000 A. were obtained for the corresponding 3-halogeno-4-benzoquinoneoximes, which were also eliminated by acids and alkalis respectively. It has been found, however (Hodgson and Nicholson, J., 1940, 1268), that 3-fluoro-4-nitrosophenol is incapable of conversion into the isomeric (unknown) 3-fluorobenzoquinone-4-oxime, and as a result it is exceedingly stable; *e.g.*, it is precipitated unchanged by acids from alkaline solutions, whereas the analogues are all converted by alkalis into the isomeric oximes; it has m. p. 161°, about mid-way between the m. p.'s of the nitroso- and the quinoneoxime forms of the analogues, does not form a picrate (cf. Hodgson, J., 1931, 1494), and is unattacked by diazomethane (cf. Hodgson, J., 1932, 1395). Moreover, the deep green colour of 3-fluoro-4-nitrosophenol, its mode of formation either by direct nitrosation or by demethylation of 3-fluoro-4-nitroso-anisole, and the failure to form a silver salt (cf. Hodgson, *loc. cit.*), all indicate a nitroso-structure. In addition, stability and relatively high m. p. are evidence of considerable polarisation [cf. Robinson, " Outline of an Electrochemical (Electronic) Theory of the Course of Organic Reactions," 1932, p. 22].



Absorption spectra of 3-*fluoro*-4-*nitrosophenol in acid, neutral, and alkaline solution.*

The absorption spectrum (see fig.) of 3-fluoro-4-nitrosophenol possesses unique features in accord with the foregoing properties. There is only one band, with peak at 3700 A. (*i.e.*, between the ionised and the un-ionised bands of the analogues), and although this band happens to be in the vicinity of the single bands given by the 3-halogeno-4-nitrosoanisoles, it is eliminated by acids and intensified by alkalis, and corresponds, therefore, to the anion. The un-ionised substance apparently absorbs very little within the wave-length range (2200—5000 A.) investigated, and at the concentration employed ($3{\cdot}2 \times 10^{-4}$ N).

The large displacement (*ca.* 300 A.) of the band towards the shorter wave-lengths, compared with the positions of the ionic bands of the analogues, indicates that relatively the electronic strain is much greater in the 3-fluoro-4-nitroso-anion, and it is suggested that the cause arises from a partial betaine (dipolar) structure of the anion (see inset), which effects almost complete closure of the external electrical field by what is virtually 5-membered-ring formation. In such a dipolar condition of the anion, the *N*-oxygen atom is prevented from becoming anionoid, and so is incapable of combination with a hydrogen ion. The nitroso-structure of the 3-fluoro-4-nitroso-anion is thus essentially preserved, whereas by contrast the nitroso-structures of the analogous anions are very unstable and readily pass over into stable quinoneoxime forms which will not revert to the original nitroso-structures.



Note. In Part I (J., 1937, 52) line 8 should read : " the 3-halogenobenzoquinone-4-oximes could not be converted directly into the isomeric nitrosophenols " (instead of oximes as printed).

Experimental.—All measurements were made by means of a Hilger ultra-violet Spekker Spectrophotometer, the absorption due to a 1, 2, or 4 cm. path of solution being compared photographically with that of a blank cell filled with the solvent used. The 3-fluoro-4-nitrosophenol was dissolved in water containing a trace of alcohol at a concentration of 46·8 mg./l., *i.e.*, $3{\cdot}2 \times 10^{-4}$ N. The pH values of the neutral, acid, and alkaline solutions were respectively 7·00, 3·24, and 10·42 as measured on a standard Cambridge pH meter.

The author gratefully acknowledges his indebtedness to Dr. H. Lowery, Principal of the South-West Essex Technical College and School of Art, and to his Research Assistant, Mr. D. Price, B.Sc., for measurement of the spectra.

TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, January 7th,* 1943.]