Infrared Absorption of Substituents in Heterocyclic Systems. Part X.[1] Amine–Imine Tautomerism by Infrared Spectroscopy: Further Examples

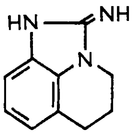
By R. T. C. Brownlee, A. R. Katritzky, and R. D. Topsom

An infrared study involving deuteration has shown that compounds previously designated as 5,6-dihydro-2-imino-1*H*,4*H*-imidazo[4,5,1-*ij*]quinoline and 1,2-dihydro-2-imino-4*H*-3,1-benzoxazin-4-one exist predominantly as their amino-tautomers.

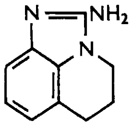
It has been shown [2,3] that a primary amino group can be identified by the presence of a triplet in the N–H stretching region of the spectrum of the partially deuterated amine. This triplet occurs because an uncoupled N–H stretching absorption, arising from the NHD group, appears between the symmetrical and antisymmetrical N–H stretching vibrations of the NH_2 group. A similar triplet cannot appear in the spectrum of a partly deuterated imine tautomeric form. We now report the application of this method to two further compounds which it had been suggested existed in the imino form.

5,6-*Dihydro-2-imino-*1H,4H-*imidazo*[4,5,1-ij]*quinoline.*—Richardson [4] concluded, from a comparison of the ultraviolet spectrum of this compound with that of its 2-methoxy- and 2-oxo-derivatives, that it existed in the imino form (I) rather than (II). In chloroform solution, there were bands at 3504 and 3412 cm.$^{-1}$ due to the antisymmetric and symmetric vibrations of the amino group. After partial deuteration, an additional band appeared at 3458 cm.$^{-1}$. Another triplet, arising from N–D stretching vibrations, was observed at 2618, 2542, and 2500 cm.$^{-1}$. The compound thus exists predominantly in the form (II) in chloroform solution.

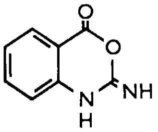
1,2-*Dihydro-2-imino-*4H-3,1-*benzoxazin-*4-*one.*—It was suggested in recent Papers [5,6] describing the preparation of this compound that it existed in the imino form (III), from a study of its ultraviolet spectrum, reactions, and infrared spectrum in the 1600—1800 cm.$^{-1}$ region. We have examined its infrared spectrum and that of a partly *N*-deuterated sample, in chloroform solution, and conclude that it exists in the amino form (IV). The partly deuterated compound showed bands at 3532, 3480, and 3422 cm.$^{-1}$, arising from the antisymmetric, uncoupled, and symmetric N–H stretching vibrations, respectively. The vibrations at 3532 and 3422 cm.$^{-1}$ occur in the undeuterated compound with no evidence for other N–H stretching modes.



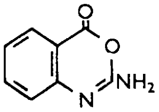
(I)



(II)



(III)



(IV)

Other Compounds.—Unsuccessful attempts were made to apply the method to substituted 2-iminothiazolidin-4-ones (cf. refs. 7 and 8) and amino-1,2,4-triazines (cf.

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ref. 9). However, refluxing of these compounds in deuterium oxide, alone or with the addition of sodium hydroxide, hydrochloric acid, or dimethyl sulphoxide, for up to 72 hr., gave no deuterium-exchanged derivative. These observations are in contrast to the generally held view of the great ease of deuterium exchange of hydrogen atoms attached to nitrogen.

EXPERIMENTAL

Both compounds were prepared as reported by the earlier workers. The imidazoquinoline had m. p. 202—203° (lit.,[4] 201—202°) (from toluene). The benzoxazinone was purified by sublimation, followed by recrystallisation from ethyl acetate, m. p. 209—212° (decomp.) (lit.,[6] 212°).

The compounds (10 mg.) were deuterated by allowing them to stand at room temperature with ethanol (0·2 ml.) and deuterium oxide (0·6 ml.) for 24 hr. The samples were vacuum-dried. The spectra were taken in 1·0-mm. sodium chloride cells, using purified chloroform, on a Perkin-Elmer model 237 grating instrument.

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