550. *The Tautomerism of* N-*Heteroaromatic Amines. Part II.* Infra-red Spectroscopic Evidence.*†

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An examination of the infra-red spectra of certain *N*-heteroaromatic amines in which tautomerism between amino- and imino-forms is possible has been made in the 3- and the 6-μ region. The results show that in chloroform solution all the samples examined exist predominantly in the amino-form.

In Part I of this series (Angyal and Angyal, *J.*, 1952, 1461) the structure of certain *N*-heteroaromatic amines such as 4-aminopyridine was considered on the basis of the available chemical evidence.

In compounds of this type tautomerism is possible between an amino- and an imino-form. It was concluded that the previous arguments in favour of the imino-form were unjustifiable in the light of modern chemical theory and that a re-examination of the problem was desirable. A semi-quantitative method was proposed for the estimation of the proportion of the tautomers in equilibrium and in the cases investigated the ratios of amino- to the imino-form were found to be greater than 10^3.

Ultra-violet absorption spectra of compounds of this type have been studied (Stock and Ewing, *J. Amer. Chem. Soc.*, 1948, **70**, 3397; Anderson and Saeger, *ibid.*, 1949, **71**, 340; Craig and Short, *J.*, 1945, 419; Turnbull, *J.*, 1945, 441; Albert and Short, *J.*, 1945, 760) but with contradictory results. The infra-red spectra of a series of amino-derivatives of pyridine, quinoline, thiazole, and pyrimidine, in which tautomerism might occur, have therefore been obtained and compared with the spectra of related compounds of known structure or in which tautomerism is not possible.

Experimental

Materials.—Aniline, α-naphthylamine, pyridine, and 2-aminopyrimidine were commercial samples; 2- and 4-aminopyridine, 4-aminoquinoline, 2-aminothiazole, and the methiodides were the samples used in Part I; 2-aminoquinoline was kindly presented by Professor A. Albert and 3-aminopyridine was prepared and presented by Dr. E. Gergely. All these substances were redistilled or recrystallised within a few hours of being examined. 1 : 2-Dihydro-2- and 1 : 4-dihydro-4-imino-1-methylpyridine were prepared according to Anderson and Saeger (*loc. cit.*). The concentrations given for these particular solutions are therfore only approximate. 2-Imino-3-methylthiazoline was prepared as described by Druey (*Helv. Chim. Acta*, 1941, **24**, 226E).

Chloroform was of B.P. quality and a solvent blank was run for each cell thickness.

Apparatus.—The spectra were recorded with a Perkin-Elmer Model 12-C single-beam instrument with rock-salt optics. This was calibrated against the bands of water vapour in the 6-μ region and against water vapour, atmospheric carbon dioxide, and ammonia in the 3-μ region (Oetjen, Kao, and Randall, *Rev. Sci. Instr.*, 1942, **13**, 515). Comparison with the spectra used for calibration indicated a resolving power of 4 cm.$^{-1}$ at 1700 cm.$^{-1}$ and 20 cm.$^{-1}$ at 3000 cm.$^{-1}$. It is well known that the position and shape of bands in the infra-red region are affected to some extent by the particular state of the material examined (Barnes *et al.*, "Infra-red Spectroscopy," New York, 1944, p. 19; Richards and Thompson, *J.*, 1947, 1248). In order therefore that any similarities or differences in the spectra of the substances investigated would be more apparent, the compounds were examined in chloroform solution. These solutions were in general approximately 10% w/w but, where necessary because of low solubility, more dilute solutions were used with a correspondingly thicker cell. Concentrations and cell thicknesses are indicated in Table 1.

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* Part I, *J.*, 1952, 1461.

† *Added in Proof.*—Dr. J. D. S. Goulden had kindly informed us, before the publication of his note (*J.*, 1952, 2939), of his results on the infra-red spectra of aminopyridines; these are in satisfactory agreement with our measurements and further confirm our conclusions.

TABLE 1. *Absorption bands in the 3-μ region.*

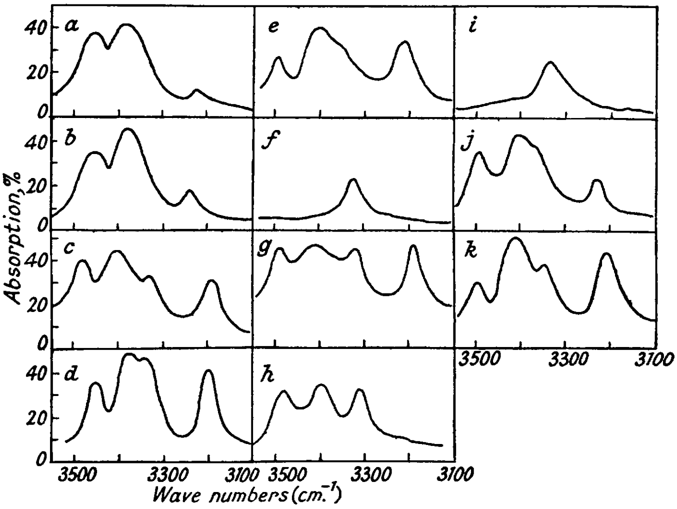
All the samples were studied in chloroform solution. Side bands are indicated in parentheses.

Compound	Absorption bands (cm.$^{-1}$)	Cell (mm.)	Concn. (% w/w)
Aniline	3228, 3383, 3452	0·025	11·0
α-Naphthylamine	3240, 3378, 3453	0·025	10·0
2-Aminopyridine	3190, (3330), 3404, 3478	0·025	9·9
3-Aminopyridine	3200, (3340), 3375, 3454	0·025	9·3
4-Aminopyridine	3216, 3405, 3492	0·25	1·0
1 : 2-Dihydro-2-imino-1-methylpyridine	3325	0·025	*ca.* 10
2-Aminoquinoline	3228, 3402, 3492	0·025	3·8
4-Aminoquinoline	3205, (3347), 3410, 3497	0·025	2·7
2-Aminopyrimidine	3188, 3319, 3410, 3488	0·050	5·0
2-Aminothiazole	3306, 3392, 3480	0·025	4·2
2-Imino-3-methyl-Δ^4-thiazoline	3335	0·025	*ca.* 10

DISCUSSION

It has been amply demonstrated that bands arising from the stretching vibrations of the hydrogen atoms against the nitrogen of amino- and imino-groups occur in the 3-μ region while the corresponding bending vibrations cause absorption in the 6-μ region. In this particular problem therefore both the 3-μ and the 6-μ region have been investigated and for convenience the results in each will be discussed separately.

FIG. 1. *Absorption spectra in the 3-μ region.*



a, Aniline. *b*, α-Naphthylamine. *c*, 2-Aminopyridine. *d*, 3-Aminopyridine. *e*, 4-Aminopyridine. *f*, 1 : 2-Dihydro-2-imino-1-methylpyridine. *g*, 2-Aminopyrimidine. *h*, 2-Aminothiazole. *i*, 2-Imino-3-methylthiazoline. *j*, 2-Aminoquinoline. *k*, 4-Aminoquinoline.

In the high-frequency region aniline and α-naphthylamine give similar spectra (Figs. 1*a* and *b*) consisting of three peaks of which the centre one is the most intense. It will be seen that the actual wave-lengths of the three bands agree closely (Table 1) and that the nucleus has only a very minor influence. Splitting of the N–H band into three components in solution has previously been noticed with amino-compounds and contrasts with the more usual two bands found in the solid state or in the pure liquid.

Because of the close resemblance of the pyridine to the benzene nucleus, it would be expected that these bands would occur in 3-aminopyridine close to the positions which they occupy in aniline and α-naphthylamine, since no tautomeric change is possible in this case. This is confirmed by an examination of that compound (Table 1) the spectrum of which agrees well with those of aniline and α-naphthylamine apart from a small unresolved band at 3340 cm.$^{-1}$ on the long wave-length side of the main centre peak. The close resemblance of the spectra of 2- and 4-aminopyridine (Figs. 1*c* and *e*) to those of the three previous compounds strongly suggests that these substances exist in the amino- rather than the imino-form and this is confirmed by comparison with the spectrum of 1 : 2-dihydro-2-imino-1-methylpyridine in which the imino-form has been stabilized. Here one finds only a single band at 3325 cm.$^{-1}$ of lower intensity (Fig. 1*f*), rather than the multiple bands of the amines.

Unfortunately, because of low solubility a satisfactory spectrum of 1 : 4-dihydro-4-imino-1-methylpyridine could not be obtained in this region, although results in the 6-μ region were clearer. However, it will be immediately obvious that 2- and 4-aminopyridine much more closely resemble the known amino-compounds.

These results have been extended by an examination of other *N*-heterocyclic amines and, of these, 2- and 4-aminoquinoline would be closest in structural similarity to the amino-pyridines. The absorptions of these compounds closely parallel those of the amino-compounds discussed above both in intensity and in the general shape and position of the bands, so that one may infer with reasonable certainty that these also must exist in the amino-form. With 2-amino-pyrimidine and -thiazole (Figs. 1*g* and *h*) the same multiple absorption bands of medium intensity occur. Some difference, however, exists between the actual wave-lengths measured for these compounds and those mentioned above. These differences are minor and are no more than would reasonably be expected considering the modified nucleus to which the groups are attached. More convincing proof of the presence of the amino-form in the substances is afforded by an inspection of the spectrum of 2-imino-3-methylthiazoline. In the same region this shows only a single band characteristic of the imino-group and quite unlike the spectra produced by 2-amino-pyrimidine and -thiazole.

In general the results in the 6—7-μ interval have supported the conclusions reached in the high-frequency region. In solution, aniline shows three strong bands in the region 1475—1700 cm.$^{-1}$ (Table 2). Those at 1500 and 1605 cm.$^{-1}$ are obviously the well-known ring vibrations of the benzene nucleus (Barnes *et al.*, *op. cit.*, p. 23) while the intensity and position of the third band (1623 cm.$^{-1}$) leave no doubt that it should be assigned to the amino-group (Williams, Hafstaedter, and Herman, *J. Chem. Phys.*, 1939, **7**, 802). The spectrum of α-naphthylamine is similar; the bands of the naphthalene nucleus occur at 1512 and 1590 cm.$^{-1}$, the latter being doubled on the long wave-length side at 1574 cm.$^{-1}$, in agreement with previous findings for naphthalene derivatives (Cannon and Sutherland, *Spectrochim. Acta*, 1951, **4**, No. 5, 373). The band of the amino-group appears at 1620 cm.$^{-1}$ close to the position recorded in aniline and with a similar intensity.

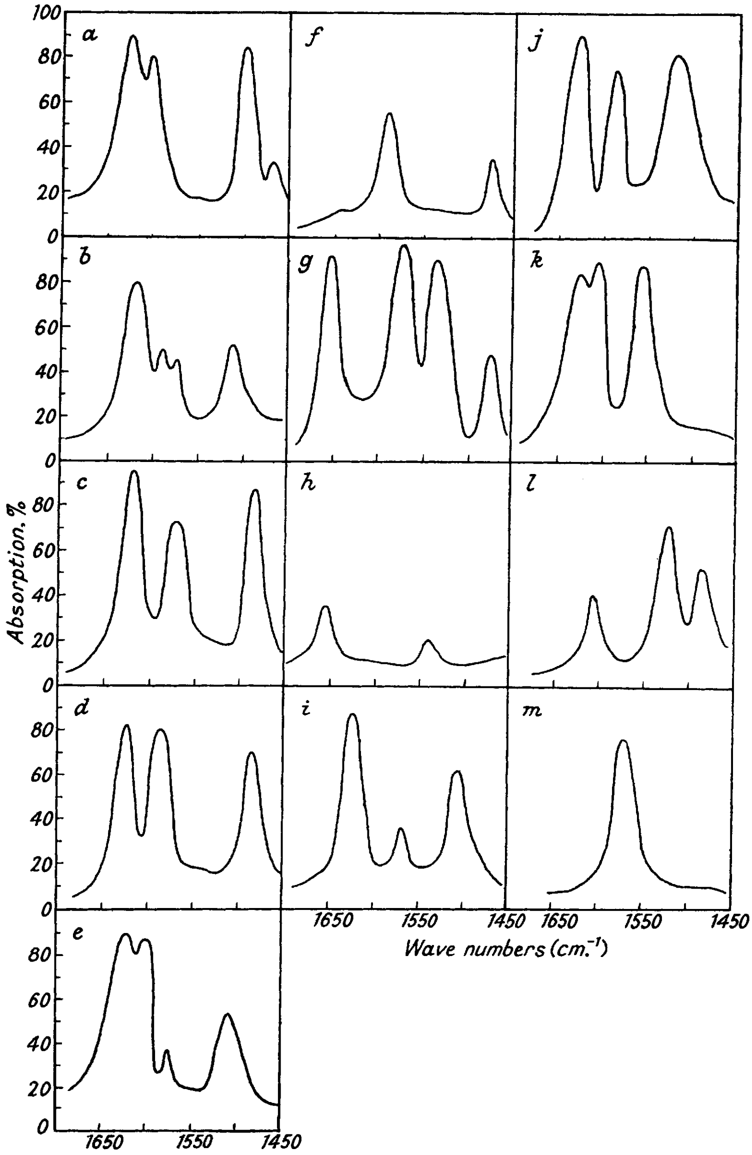
TABLE 2. *Absorption bands in the* 6-μ *region.*

(Cell thicknesses and concns. are given in Table I.)

Compound	Absorption bands (cm.$^{-1}$)
Aniline	1470, 1500, 1605, 1623
α-Naphthylamine	1512, 1574, 1590, 1620
2-Aminopyridine	1487, 1570, 1619
3-Aminopyridine	1485, 1586, 1623
4-Aminopyridine	1508, 1572, 1601, 1626
Pyridine	1475, 1590
1 : 2-Dihydro-2-imino-1-methylpyridine	1475, 1534, 1572, 1652
1 : 4-Dihydro-4-imino-1-methylpyridine	1542, 1655
2-Aminoquinoline	1506, 1568, 1622
4-Aminoquinoline	1518,1587,1629
2-Aminopyrimidine	1562, 1605, 1624
2-Aminothiazole	1486, 1523, 1605
2-Imino-3-methylthiazoline	1582

Examination of pyridine under the same conditions shows the presence of two bands at 1475 and 1590 cm.$^{-1}$ which are apparently due to vibrations of atoms in the ring. Some controversy, however, seems to exist as to the correct assignment of the 1590-cm.$^{-1}$ band. In the pure liquid this band has been measured at 1580 cm.$^{-1}$ by one group of investigators (Randall, Fowler, Fuson, and Dangl, " Infra-red Determination of Organic Structures," New York, 1949, p. 32) and assigned to the C=N group. This would be a usual position for C=N in a conjugated system and would agree with conclusions reached by an examination of pyridine, quinoline, etc., by Raman spectroscopy (Hibben, "The Raman Effect and its Chemical Applications," New York, 1939, p. 294). On the other hand, Brownlie (*J.*, 1950, 3062) assigns bands around 1580 cm.$^{-1}$ in pyrimidine derivatives to C=C and bands at about 1640—1650 cm.$^{-1}$ to C=N, which would be the position of such groups in an unconjugated system. This seems rather unusual and another interpretation (Blout,

FIG. 2. *Absorption spectra in the* 6-μ *region.*



a, Aniline. *b*, α-Naphthylamine. *c*, 2-Aminopyridine. *d*, 3-Aminopyridine. *e*, 4-Aminopyridine. *f*, Pyridine. *g*, 1 : 2-Dihydro-2-imino-1-methylpyridine. *h*, 1 : 4-Dihydro-4-imino-1-methylpyridine. *i*, 2-Aminoquinoline. *j*, 4-Aminoquinoline. *k*, 2-Aminopyrimidine. *l*, 2-Aminothiazole. *m*, 2-Imino-3-methylthiazoline.

Fields, and Karplus, *J. Amer. Chem. Soc.*, 1948, **70**, 194), that in conjugated systems involving both C═C and C═N no absolute assignment can be made, seems more logical. This is particularly the case since the bands due to C═C and C═N groups occur close together when in unconjugated systems and are similarly affected by conjugation. In such circumstances the normal vibrations of the system cannot be identified with the vibration of particular bonds alone, and the bands in the region in question should more correctly be assigned to the nucleus as a whole.

In agreement with these conclusions Short and Thompson (*J.*, 1952, 168) have assigned bands at 1569 and 1610 cm.$^{-1}$ in solid pyrimidine to vibrations of the ring, and these values lie close to those recorded by us for 2-aminopyrimidine in solution.

The spectrum of 3-aminopyridine combines the features of both pyridine and aniline. The ring vibrations are found at 1586 and 1485 cm.$^{-1}$, and the band of the amino-group at 1623 cm.$^{-1}$, as in aniline. The last band is characteristically stronger than the accompanying ring vibrations (Fig. 2*d*). The spectra of the 2- and the 4-amino-isomer are similar with strong bands at 1626 and 1619 cm.$^{-1}$ respectively, which suggest amino-groups, and other bands corresponding closely to the ring vibrations of pyridine and 3-aminopyridine. In the case of 4-aminopyridine it will be observed that one of the ring bands is doubled at 1601 and 1572 cm.$^{-1}$, but this is not unusual, having been observed in other pyridine derivatives (Cannon and Sutherland, *loc. cit.*, p. 377). Comparison with the two reference compounds 1 : 2-dihydro-2- and 1 : 4-dihydro-4-imino-1-methylpyridine favours the amino-form, for, not only do these compounds give strong bands which have shifted to the region 1650—1660 cm.$^{-1}$ (Table 2) and are presumably due to the group ═N–H, but also the ring vibrations appear to be somewhat different. It should be remembered when comparing these spectra that the apparent low intensity of the bands of 1 : 4-dihydro-4-imino-1-methylpyridine is due only to the concentration used.

The isomers 2- and 4-aminoquinoline are very similar, giving bands which resemble the ring vibrations of the pyridine compounds and strong bands at 1622 and 1629 cm.$^{-1}$ which are difficult to assign to other than amino-groups. For 2-aminopyrimidine the ring vibrations differ somewhat, owing to the increasing effect of the C═N groups, but the amino-band shows strongly at 1624 cm.$^{-1}$ and indicates the presence of the amino-form. Short and Thompson (*loc. cit.*) have arrived at the same conclusion from an examination of the solid material. The results for 2-aminothiazole are somewhat difficult to interpret in this region where the influence of the different nucleus is more pronounced. While the band at 1605 cm.$^{-1}$ seems likely to be due to an amino-group rather than an imino-group, the best evidence for the presence of the amino-form in 2-aminothiazole is in the 3-μ region.

In general it may be concluded that the compounds considered, at least in solution, exist in the amino- rather than the imino-form.

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