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Electron Diffraction Studies on the Molecular Structures of Pyridine and Furan

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Electron diffraction studies have been carried out on the structures of pyridine and furan. The results have been compared with those obtained from the microwave spectra [1,2]. The obtained structure parameters found are summarized in Tables 1 and 2.

Microwave studies have led to very accurate determinations of the molecular parameters of pyridine [1], and furan [2]. An independent electron diffraction study using the sector method [3] promised to provide valuable informations as to the molecular structures of the compounds. It would also determine whether the two methods, which are quite different in principle, lead to the same results. The electron diffraction studies were carried out on the same samples used in the microwave work.

Pyridine. Fig. 1 shows the intensity curve of pyridine obtained after subtraction of the background. Various different radial distribution curves have been calculated both from the undamped intensity curve and from intensity curves multiplied by various damping factors. Fig. 2 shows the radial distribution curve calculated using a damping factor of $e^{-0.0009s^2}$.

Each of the peaks in the radial distribution curve is composed of contributions from two or more different distances. For example, the main peak at approximately 1.38 Å is built up of contributions from the C-C bonds and the C-N bonds; the corresponding distances are too close together to be separated. In this comparison of the microwave and the electron diffraction results, therefore, average values are involved.

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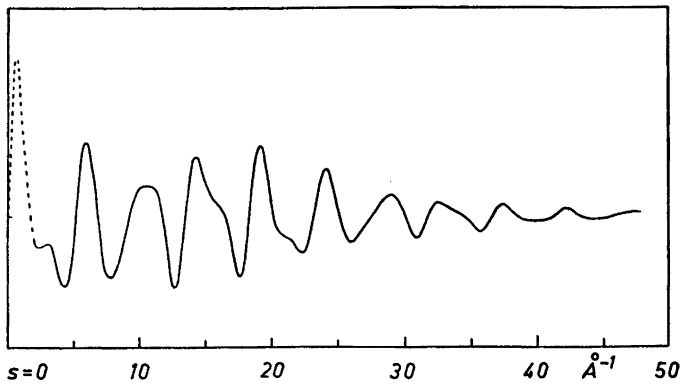

Fig. 1. Intensity curve for pyridine.

Table 1. Mean distances in pyridine obtained from the microwave spectra and from the electron diffraction studies.

Distances	H_2-C_2 H_3-C_3 H_4-C_4	$N-C_2$ C_2-C_3 C_3-C_4	H_2-N H_2-C_3 H_3-C_2 H_3-C_4 H_4-C_3	$N-C_3$ C_2-C_4 C_2-C_6 C_3-C_5	$N-C_4$ C_2-C_5	H_2-C_6 H_2-C_4 H_3-N H_3-C_5 H_4-C_2	H_2-C_5 H_3-C_6 H_4-N
Microwave model V	1.081	1.377	2.137	2.384	2.753	3.358	3.821
Electron dif. values	1.078	1.377	2.141	2.384	2.748	3.356	3.802

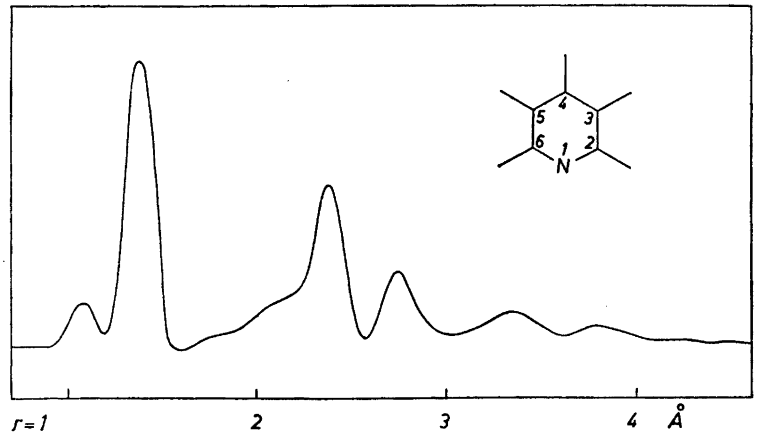

Fig. 2. Radial distribution curve for pyridine.

In Table 1 the best electron diffraction data have been listed, together with the data calculated from the best microwave model[1]. All of the distances contributing to the mean distances are listed in the first row. The numbering of the atoms can be seen from Fig. 2. The correspondence between the values obtained from the two different methods is extraordinarily good; it is, as a matter of fact, somewhat better than one would expect in view of the probable errors of the methods. Because of the many, indeed very small, sources of uncertainty it is difficult to make a definite statement concerning the probable error of the various distances obtained from the electron diffraction studies. However, the following qualitative discussion may be helpful. The peaks at 1.078, 2.384 and 2.748 Å seem all to be highly reproducible. The various ways of approaching the problem seem to give very nearly the same values for the average distances corresponding to these peaks. The study of the intensity curve and of the radial distribution curves based upon various damping factors give essentially the same values, *i.e.* only a variation of a few thousandths of an Ångstrom. The maximum of the peak at 2.141 Å is not determined with this high accuracy, however. The peak is so close to its neighbour at 2.384 Å that a different procedure has to be applied. The position of the maximum is reproduced with a maximum error of 0.012 Å. The peaks at 3.356 and 3.802 Å are small and might, therefore, not be expected to be determined very accurately. On the other hand they are well resolved, and the deviation between the microwave and the electron diffraction values is negligible in the first case and only about 0.5 % in the second case.

The peak at 1.377 Å seems on the first inspection to lead to some difficulties. Although this peak is the predominating one there is a definite increase in the position of its maximum when the damping factor increases. The undamped intensity curve leads to a value of 1.371 Å, and the value increases to a limit of 1.377 Å when the damping factor is increased. This effect is very reproducible, but so small as to raise questions as to experimental errors, such as magnetic fields in the apparatus, for example. The effect on the most pronounced peak in other compounds has, therefore, been studied. In addition to pyridine the effect was observed only in the case of furan. The explanation is probably the following: Every distance contributes to the intensity curve by a damped sine-like function. The damping is dependent upon the variation in the distances because of molecular vibrations, so that the "stiffer" the distance the less the damping. Now, the various bonds contributing to the peak under discussion have different force constants. If the plausible assumption is made that the shorter bonds are the stiffer ones, these bonds should dominate the outer range of the intensity curve. Accordingly the radial distribution curves based upon undamped intensity curves should have the main peak shifted toward small r-values. The artificial damping has a tendency to equalize the contribution from the various bonds. This is the reason for believing the average distance calculated from the damped intensity curve to be the best value.

Furan. Fig. 3 is the intensity curve and Fig. 4 the radial distribution curve for furan. Various radial distribution curves were also calculated for furan by the same procedure as was used for pyridine. The results are summarized in Table 2, where the best electron diffraction data are compared with the two

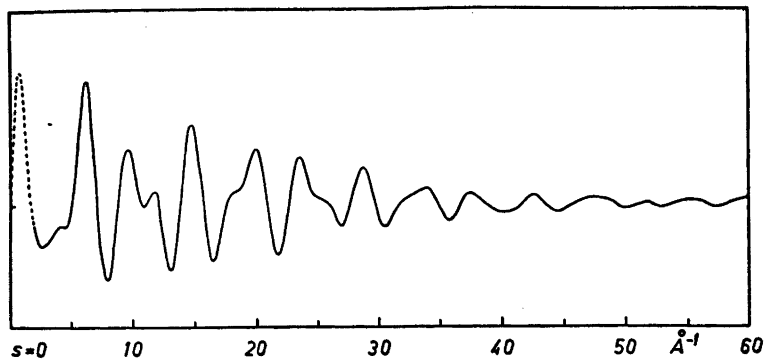

Fig. 3. Intensity curve for furan.

best models obtained from the microwave studies by Bak, Hansen and Rastrup-Andersen [2]. From the electron diffraction work it is impossible to distinguish between the two microwave models. Unfortunately, the average distance

Table 2. Mean distances in furan obtained from the microwave spectra and from the electron diffraction studies.

Distances	H_2-C_2 H_3-C_3	$O-C_2$ C_2-C_3 C_3-C_4	H_2-O H_2-C_3 H_3-C_2 H_3-C_4	$O-C_3$ C_2-C_4 C_2-C_5	H_2-C_4 H_2-C_5 H_3-C_5 H_3-O
Microwave model III	1.075	1.378	2.186	2.229	3.260
» IV	1.075	1.378	2.185	2.228	3.261
Electron diffraction	1.075	1.377		2.230	3.272

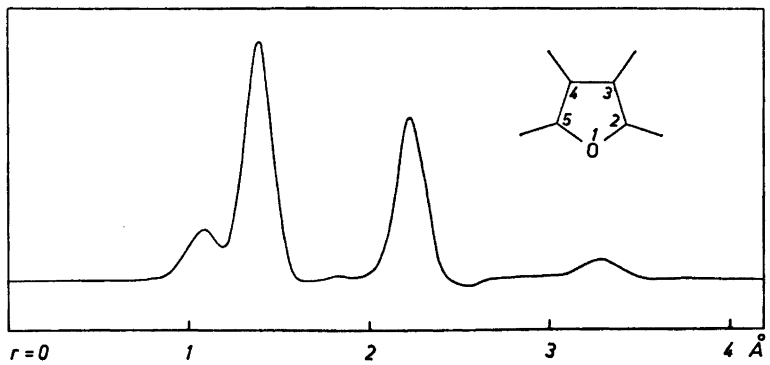

Fig. 4. Radial distribution curve for furan.

from hydrogen to carbon, and hydrogen to oxygen through one angle cannot be determined, as it is too close to the r-value of the peak at 2.230 Å. As mentioned above, in this case as well the position of the main peak is dependent upon the artificial damping factor. The peak occurs in the undamped case at 1.370 Å.

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