

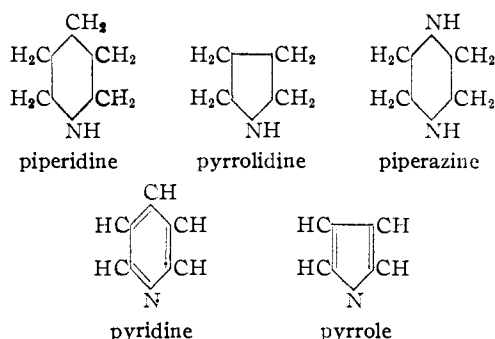
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MOUNT HOLYOKE COLLEGE]

The Vacuum Ultraviolet Spectra of Cyclic Compounds. III. Amines<sup>1</sup>BY LUCY W. PICKETT, MARY E. CORNING, GRACE M. WIEDER, DOROTHY A. SEMENOW AND  
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The far ultraviolet absorption spectra (40,000–65,000 cm.<sup>-1</sup>) of piperidine, pyrrolidine, piperazine, pyridine and pyrrole have been measured in vapor phase by means of a fluorite prism vacuum spectrograph and a Beckman spectrophotometer. The effects of cyclization, ring size and number of nitrogen atoms on the spectra of the saturated amines and related compounds are discussed. The band positions for the aromatic amines are compared with values calculated by a molecular orbital method. The effect of solvents on the observed transitions has been found and the base strength of this group of compounds has been redetermined for comparison with the spectral data.

The earlier papers of this series<sup>2</sup> discuss the far ultraviolet absorption spectra of five- and six-membered ring hydrocarbons and ethers. The five compounds presented here are



Three of these are saturated secondary amines whose absorption in this region may be attributed to the non-bonding electrons of the nitrogen atom, while in the latter two conjugation effects with charge displacement around the ring are important. The selection of these five molecules afforded an opportunity to compare (a) cyclic with non-cyclic amines, (b) nitrogen and the corresponding oxygen compounds,<sup>2</sup> (c) five- with six-membered rings, (d) single with double nitrogen substitution and (e) the effect of a conjugated system on the spectra. Furthermore since these rings may be found as structural units in biological compounds of growing importance, a knowledge of their absorption spectra was considered to be of value.

While some earlier studies have been made of piperidine,<sup>3</sup> piperazine<sup>4</sup> and pyridine<sup>5</sup> in the quartz ultraviolet region, little information is available at the shorter wave lengths except for a note on pyridine by Price and Walsh.<sup>6</sup> These authors<sup>7</sup> as well as Scheibe and Grieneisen<sup>8</sup> have reported the spectrum of pyrrole in the vacuum ultraviolet region

(1) This work was supported by the ONR under contract N8onr-74100, NR-055-160.

(2) L. W. Pickett, M. Muntz and E. M. McPherson, *THIS JOURNAL*, **73**, 4862 (1951); L. W. Pickett, N. J. Hoeflich and T. C. Liu, *ibid.*, **73**, 4865 (1951).

(3) W. N. Hartley, *J. Chem. Soc.*, **47**, 685 (1885); J. Purvis, *ibid.*, **97**, 692, 1035 (1910); E. Herrmann, *Z. wiss. Photochem.*, **18**, 253 (1919); H. Ley and B. Arends, *Z. physik. Chem.*, **B17**, 177 (1932).

(4) J. Purvis, *J. Chem. Soc.*, **103**, 2283 (1913).

(5) F. Baker and E. Baly, *ibid.*, **91**, 1122 (1907); J. Purvis and E. Herrmann, *ref. 3*; H. Spouer and H. Stücklen, *J. Chem. Phys.*, **14**, 101 (1946).

(6) W. Price and A. D. Walsh, *Proc. Roy. Soc. (London)*, **A191**, 22 (1947).

(7) W. Price and A. D. Walsh, *ibid.*, **A179**, 201 (1941).

(8) G. Scheibe and H. Grieneisen, *Z. physik. Chem.*, **B25**, 52 (1934).

without, however, giving measurements of intensity. No record has been found of spectral measurements of pyrrolidine.

## Experimental

**Purification of Compounds.**—In general, samples of these compounds were secured from the best sources available and, after preliminary distillation or purification, were dried over sodium hydroxide and distilled through a 32-cm. Fenske column in an atmosphere of nitrogen. A middle fraction was immediately used for the measurements. In one measurement of piperidine and of pyrrolidine, the fraction from the Fenske distillation was collected in a tube filled with dry calcium oxide and directly distilled from this in vacuum into the sample tube attached to the absorption cell, while the measurement itself involved another vacuum distillation. In all cases materials from two sources, separately purified, were used for the measurements. Piperazine, a solid, was dried in a vacuum oven and sublimed in vacuum. The sources and physical properties are listed in Table I.

TABLE I

| Substance   | Sources   | B.p.,<br>°C. | n <sub>D</sub> <sup>20</sup> |
|-------------|---|--------------|------------------------------|
| Piperidine  | Eastman Kodak<br>Eimer and Amend  | 106          | 1.4530                       |
| Pyridine    | Baker Analyzed  | 115.3        |                              |
| Pyrrolidine | Zinc chloride purification in lab. <sup>9</sup><br>Synthesis, this lab. <sup>10</sup><br>du Pont Co. (courtesy of Electrochemicals Dept.) | 86           | 1.4430                       |
| Pyrrole     | Eimer and Amend<br>Matheson Co.   | 130          | 1.5097                       |
| Piperazine  | Eimer and Amend<br>Bios Co.   |              |                              |

**Spectral Measurements.**—A fluorite prism vacuum spectrograph was used to measure the compounds in the form of flowing vapors at measured pressures, and values of molar extinction coefficient were calculated from microphotometer records of the photographs. These methods, which have been described in earlier papers,<sup>2,11</sup> were supplemented by solution and vapor phase studies with a Beckman ultraviolet spectrophotometer. Each curve represents more than a hundred experimental points. An average deviation of 0.03 or less in log  $\epsilon$  was found in most cases for values at the same wave length over a range of pressures. In the spectral region common to both Beckman and vacuum instruments the agreement was good. Intensity measurements for pyrrole, however, could not be duplicated.

In the case of piperazine, only the top of the band could be observed because the vapor pressure of this compound is low at room temperature and not measurable on the gage used. In order to measure the vapor concentration, a

(9) J. Heap, W. Jones and J. Speakman, *THIS JOURNAL*, **43**, 1936 (1921).

(10) This sample was kindly prepared by M. K. Glover under direction of Dr. M. L. Sherrill by hydrolysis of N-p-toluenesulfonylpyrrolidine with 48% hydrobromic acid.

(11) A. J. Harrison, C. L. Gaddis and E. M. Coffin, *J. Chem. Phys.*, **18**, 221 (1950).

sampling bulb of known volume (1064 ml.) was attached to the flowing vapor system near the absorption cell and a sample collected just before the exposure when equilibrium had been established. The vapor was condensed at  $-78^\circ$  in a small collecting bulb and the piperazine titrated by a micro technique. A comparison was made between this method of determining vapor concentration and pressure measurements with the modified McLeod gage with pyrrolidine as test substance. The concentrations agreed within 5%, the lower value resulting from the gage reading.

**Determination of Base Strength of Amines.**—The base strength of the amines was found by spectrophotometric and potentiometric methods. Because of the difference in absorption of molecules and ions it was possible to use the former method for piperidine, pyrrolidine and pyridine. The equilibrium constant  $K_B$ , defined as  $a(\text{BH}^+) a(\text{OH}^-)/a(\text{B})$  where  $a(\text{BH}^+)$  represents the activity of the ion and  $a(\text{B})$  that of the molecule, was determined in most cases by finding the  $pH$  and the optical density of a buffered solution which contained a mixture of molecular and ionic forms.

The  $pH$  was measured with a Beckman  $pH$  meter, model G, using glass and calomel electrodes. For measurements in the region of high  $pH$ , a special glass electrode designed for this purpose was used. Each set of measurements was standardized by comparison with two buffer solutions in a similar  $pH$  range and the readings are considered to be reliable to 0.02  $pH$  unit. The activity of the hydroxyl ion was found as  $K_w/a_H$  where  $K_w$  was taken as  $1.008 \times 10^{-14}$  at zero ionic strength. The measurements were made at  $25^\circ$  unless otherwise indicated.

The optical densities were obtained with a Beckman spectrophotometer, model DU. Aqueous solutions of hydrochloric acid, sodium hydroxide, and buffer solutions of boric acid and of a sodium acetate-acetic acid mixture were made, with care to exclude carbon dioxide, for use as solvents. After preliminary measurements of a number of solutions of varying  $pH$  in order to find the limiting values indicating that only one species, either ion or molecule, was present, and to determine the wave lengths where the ion and molecule showed the greatest difference in extinction coefficient, comparison studies were made using the same concentration of amine in acid, alkaline, and buffer solutions. The following relation then existed between the optical densities, or absorbance  $A$ , corrected for cell and solvent, and the concentrations of ion and molecule

$$\frac{A(\text{B}) - A(\text{mixture}^+)}{A(\text{mixture}^+) - A(\text{B}^+)} = \frac{c(\text{B}^+)}{c(\text{B})}$$

Activity coefficients were estimated from the approximate Debye-Hückel expression.

A potentiometric method was used also in the case of piperidine, pyrrolidine and piperazine. Values of  $pK_B$  were found from the titration curve obtained by measuring the  $pH$  as described above during a titration with standard hydrochloric acid (0.1 or 0.02  $N$ ). The curve for piperazine showed two distinct end-points.

### Discussion of Results

The values of molar extinction coefficient,  $\epsilon = (1/cl) \log I_0/I$ , where  $l$  is path length in cm. and  $c$  is molar concentration, are shown in Fig. 1 for the saturated compounds, while in Fig. 2,  $\log \epsilon$  is shown for piperidine in comparison with its unsaturated analog pyridine. The latter is so much more absorptive that the two could not well be presented on the same scale of epsilon. As is best seen from the logarithmic curve, piperidine has a low-lying step-out followed by a comparatively intense band on whose slope is a series of narrow bands with positions shown in Fig. 1. The broad band maximum occurs just below 2000 Å. and is followed by a minimum and rise to another maximum below 1600 Å. The position and general character of the bands are similar to diethylamine<sup>12</sup> with, however, a slight displacement toward the visible and slight increase

(12) A. J. Harrison, E. M. Coffin and E. Tannenbaum, *J. Chem. Phys.*, in press.

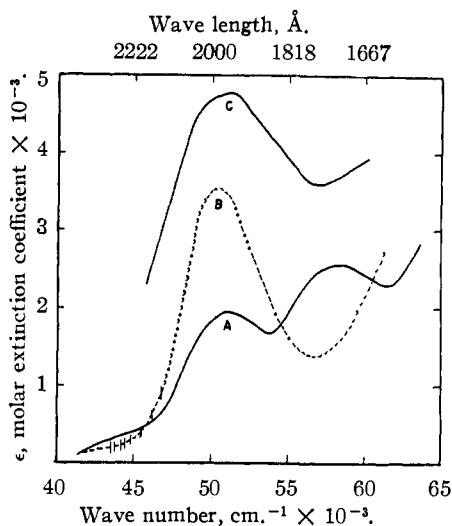


Fig. 1.—Ultraviolet absorption spectra: A, pyrrolidine; B, piperidine; C, piperazine.

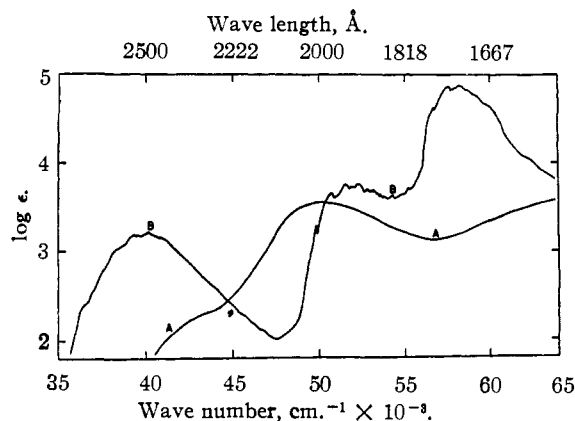


Fig. 2.—Ultraviolet absorption spectra: A, piperidine; B, pyridine.

of intensity for the cyclic compound. This would indicate that in the secondary amines, where the environment of the nitrogen atom is similar, and where strain is not involved, cyclization has but a small effect on the absorption curve.

The curve of the five-membered ring is however quite different from that of the six-membered ring compound. Anomalies have been observed in the spectra of five-membered rings in the case of unsaturated hydrocarbons and ethers<sup>2</sup> also. Two distinct bands of lower intensity are found in the pyrrolidine and in tetrahydrofuran in place of one (with an overlapping stepout) in the corresponding six-membered rings. This suggests that the splitting may be characteristic and is related to the bond angle and the probable strain in these compounds.

In contrast to ammonia and monoethylamine and in striking contrast to the cyclic ethers, the bands of the cyclic saturated amines show little evidence of vibrational structure. There are a few very narrow bands on the upward slope of the first band of piperidine, and in pyrrolidine there is evidence of very shallow indistinct bands superimposed on the bands in this region.

The effect of two nitrogen atoms is seen in piperazine where the increase in the intensity and

breadth of the band maximum is reasonable in view of the doubled probability of excitation in the diacid base. This is even more evident from the comparison of oscillator strengths shown in Table II and calculated from the area under the bands between the limits shown ( $f = 4.32 \times 10^{-9} \int \epsilon d\nu$ ). The comparison of the data would indicate that the oscillator strength associated with the excitation of a nitrogen non-bonding electron is of the order of 0.1, though this may be distributed between two transitions.

TABLE II  
OSCILLATOR STRENGTH OF BANDS

| Substance   | Wave number range<br>in $\text{cm.}^{-1}$ | $f$ -value |
|-------------|---|------------|
| Piperidine  | 40,000-56,700                             | 0.11       |
| Pyrrolidine | 40,000-53,500                             | .05        |
|             | 53,500-61,700                             | .08        |
| Piperazine  | 47,000-57,100 <sup>a</sup>                | .20        |
| Pyridine    | 36,000-47,800                             | .04        |
|             | 47,800-54,500                             | .10        |
|             | 54,500-64,000                             | 1.3        |

<sup>a</sup> Band extends to lower wave numbers but not measurable because of low vapor pressure.

It is reasonable to expect in the case of the saturated amines an excitation essentially atomic-like and hence the first member of a Rydberg series. There is difficulty of nomenclature since the lone-pair electrons, which could be described as  $2p_z$  if the surrounding groups were planar or as  $2s$  if the bond angles were  $90^\circ$ , are neither, but are perhaps in a hybrid orbital,  $a(2s) + b(2p)$  where  $b > a$ . If a transition to a  $3s$  orbital is ascribed to one of the bands in this region, there is evident in these compounds, either as a stepout or separately, a second band, too close to represent reasonably a transition to a  $3d$  orbital. It seems possible that the second band represents a transition from a non-bonding orbital to an antibonding orbital of a N-C bond and is similar to the N-Q transitions discussed by Mulliken<sup>13</sup> for alkyl halides. There would be a displacement of negative charge from the nitrogen toward the carbon atoms.

In contrast to the saturated amines, pyrrole and pyridine have very different spectra as their aromatic structure would imply. The position of the bands of pyrrole is recorded in Table III. There are three band systems in pyrrole as was observed by Scheibe.<sup>8</sup> Similar values were found for the first and third of these, but the second group which he reports as an unresolved maximum was observed in this work as a group of well defined bands similar in appearance to the band system of furan beginning at  $52,220 \text{ cm.}^{-1}$ . The band believed to be the 0-0 band in this second group in pyrrole is at  $54,670 \text{ cm.}^{-1}$ . The first band systems are similar in position in furan and pyrrole, while the third is found at lower wave numbers in pyrrole.

The individual bands in the first group of pyrrole are few in number and diffuse except for the strongest. Those of the second band system fall into a pattern which indicates that excited state vibra-

TABLE III  
BAND POSITIONS IN  $10^{-1} \text{ CM.}^{-1}$  (WAVES PER MM.)

| PYRROLE |                    |         |
|---------|--------------------|---------|
| Group 1 | Group 2            | Group 3 |
| 4625 wa | 5456 vw            | 5740 sa |
| 4739 s  | 5467 vs            | 5796 w  |
| 4840 m  | 5480 vw            | 5802 w  |
| 4879 m  | 5540 vw            | 5812 s  |
|         | 5554 m             | 5825 m  |
|         | 5574 ms            | 5827 s  |
|         | 5609 mw            | 5845 s  |
|         | 5618 mw            | 5860 m  |
|         | 5643 w             | 5866 w  |
|         | 5662 m             | 5876 mw |
|         | 5680 m             | 5885 m  |
| a       | position uncertain | 5892 ms |
| w       | weak               | 5902 m  |
| m       | medium             | 5918 m  |
| vs      | very strong        | 5930 ms |

tional frequencies are 870, 1070, 1425 and  $1510 \text{ cm.}^{-1}$  with the possible addition of  $730 \text{ cm.}^{-1}$ . These correspond to ground state frequencies observed in the Raman and infrared spectra,<sup>14</sup> and the first three are comparable to those excited in the spectrum of furan. There are weak bands which apparently come from higher vibrational levels of the ground electronic state. The lower overtones and combinations which would be expected are present but the higher ones are covered by the third band system which is of much higher intensity. The band which may be the first of this system coincides with the nitrogen emission lines used as standards so that its exact position is uncertain, while the hydrogen line spectrum obscures the higher vibrational bands. However, comparable frequencies to those of the second band system may be observed although the pattern is more complex.

The intensities of the pyrrole bands are higher than those of furan especially in the case of the first and third systems. However, the uncertainty in molar extinction coefficients is far greater for pyrrole than for any of the others studied in this Laboratory.

The spectrum of pyridine is very similar to that of benzene. Since the bands in the near ultraviolet region have been carefully studied by Sponer and co-workers,<sup>5</sup> only the band enveloped in this region is shown. This was determined in vapor state with the Beckman spectrophotometer without attempt to resolve the fine structure. While this band is appreciably more intense than the symmetry forbidden benzene band in similar position, as is reasonable, the two distinct band systems at shorter wave length are remarkably similar both in position and intensity to those of benzene.<sup>2</sup> The displacement is about  $1400 \text{ cm.}^{-1}$  toward shorter wave lengths. The marked similarity justifies the treatment of pyridine as a perturbation of benzene.

Some calculations by a molecular orbital (LCAO) method were made of the energy levels and charge distribution for the molecules of pyrrole and pyridine. These are similar to those originally made to determine charge distribution in the ground state

(13) R. S. Mulliken, *J. Chem. Phys.*, **8**, 382 (1940); *Phys. Rev.*, **61**, 277 (1942).

(14) R. C. Lord and F. A. Miller, *J. Chem. Phys.*, **10**, 328 (1942) (earlier references in this paper); J. Lecomte, *Bull. soc. chim. (Mem.)*, **415** (1946); J. Garach and J. Lecomte, *Compt. rend.*, **222**, 74 (1946).

by Wheland and Pauling<sup>15</sup> and others. Nordheim and Sponer<sup>16</sup> have calculated excited state levels for pyridine and picolines. In all of these calculations the problem is treated like benzene as one of six  $\pi$ -electrons. In pyrrole the lone-pair electrons are assumed to form part of this sextet while in pyridine the lone-pair electrons are differently oriented and the nitrogen contributes only one  $\pi$ -electron.

The standard method of approach is to express six molecular orbitals as linear combinations of atomic orbitals and to find solutions for the set of secular equations  $\sum c_{jk}(H_{mk} - S_{mk}E_j) = 0$ , where  $H_{mk} = \int \psi_m H \psi_k dr$ ;  $S_{mk} = \int \psi_m \psi_k dr$ . If  $\alpha$  represents the coulomb integral for carbon,  $\alpha + \delta\beta$  was used for the nitrogen atom and for the carbon atoms immediately adjoining this, with the value of  $\delta$  in the second case  $1/8$  to  $1/10$  of the former.

The orbital energies and the energy of the first four transitions together with the resulting charge distribution in the normal state are shown in Table IV. In these calculations the overlap integral was taken as 0 and the assumptions are shown in regard to the coulomb integral of the nitrogen and neighboring carbon atoms. The work in some parts repeats those of the earlier authors. Other calculations were carried out, using values of overlap integral for the C-N bond of 0.20 for pyridine, 0.18 for pyrrole and for the C-C bond 0.25, but the agreement with observed values was less satisfactory.

TABLE IV

CALCULATED AND OBSERVED TRANSITION ENERGIES OF PYRIDINE AND PYRROLE

| Assumptions                          | $\delta N$ | Pyridine                                |   | Pyrrole |        |
|--------------------------------------|------------|---|---|---------|--------|
|                                      |            | 1                                       | 2                                       | 1       | 2      |
| $\delta C\alpha$                     | 0.125      | 0.2                                     | 0.125                                   | 0.2     | 0.2    |
| Charge distribution                  | N          | 1.339                                   | 1.592                                   | 1.497   | 1.707  |
|                                      | C $\alpha$ | 0.904                                   | 0.831                                   | 1.122   | 1.081  |
|                                      | C $\beta$  | .975                                    | .960                                    | 1.129   | 1.065  |
|                                      | C $\gamma$ | .904                                    | .824                                    |         |        |
| Orbital energies                     |            | 1.857                                   | 1.794                                   |         |        |
| ( $\alpha - E$ ) in units            |            | 0.934                                   | 0.905                                   | 1.585   | 1.567  |
| of $\beta$                           |            | 0.659                                   | 0.408                                   | 1.224   | 0.977  |
|                                      |            | -1.064                                  | -1.105                                  | -0.710  | -0.766 |
|                                      |            | -1.319                                  | -1.510                                  | -1.000  | -1.264 |
|                                      |            | -2.322                                  | -2.893                                  | -2.348  | -2.908 |
| Transition energies                  |            | 1.723                                   | 1.513                                   | 1.934   | 1.743  |
| calculated in units                  |            | 1.978                                   | 1.918                                   | 2.224   | 2.241  |
| of $\beta$ for lowest energy changes |            | 1.998                                   | 2.010                                   | 2.295   | 2.333  |
|                                      |            | 2.253                                   | 2.415                                   | 2.585   | 2.831  |
| Transition energies                  |            | 38350 cm. <sup>-1</sup> or 1.53 $\beta$ | 46250 cm. <sup>-1</sup> or 1.85 $\beta$ |         |        |
| observed assuming $\beta = 3.1$ e.v. |            | 49800                                   | 1.99                                    | 54560   | 2.18   |
|                                      |            | 56000                                   | 2.24                                    | 57400   | 2.30   |

The four calculated transitions should be symmetry allowed on the basis of  $C_{2v}$  symmetry of the molecules. However, the calculations would be expected to give only the average locations of singlet and triplet levels in each case and there are various approximations made in this type of calculation. However, it seemed of interest to compare the observed transitions with those calculated as is shown in Table IV.

**Solvent Effects.**—The effect of solvent on the spectra of these compounds is of interest, not only

(15) G. W. Wheland and L. Pauling, *THIS JOURNAL*, **57**, 2086 (1935); H. C. Longuet-Higgins and C. A. Coulson, *Trans. Faraday Soc.*, **43**, 87 (1947).

(16) G. P. Nordheim and H. Sponer, *J. Chem. Phys.*, **20**, 285 (1952).

because the displacement is in the opposite direction from the more commonly observed effects but because it provides evidence for the band assignment. In all of the saturated amines a displacement to shorter wave lengths was found. This is small for a non-polar solvent such as isoöctane, greater for polar solvents, while in acid solution no appreciable absorption is found above 2000 Å. For example, the molar extinction coefficients of pyrrolidine at 2200 Å. are: vapor 429, isoöctane 370, 0.01 *N* NaOH 85, 0.01 *N* HCl negligible. Since in the acid solution, the non-bonding electrons of the free amine have formed a stable bond with the proton, this would indicate that the bands in these compounds at 2000 Å. or above originate in the lone-pair electrons rather than in those of the C-N bond.

The 2500 Å. band of pyridine does not, however, disappear but rather becomes more intense in acid solution, additional evidence that this excitation does not primarily concern the lone-pair electrons. Pyrrole is unstable in acid solution.

Other workers with piperidine have noted the appearance of a band in acid solution<sup>3,4</sup> at 2550 Å. and there has been discussion<sup>17</sup> as to whether or not this was due to pyridine as a persistent impurity. Such a band was noted in some of our measurements and its variation in intensity in different samples of piperidine indicated its nature as an impurity. The original reason for the study of pyridine in fact was to identify this possible impurity, and the conclusion reached was that the substance present in the piperidine was not pyridine. Studies of a sample of piperidine in aqueous solutions of varying *pH* values enabled further information to be obtained about this very persistent impurity in that its *pK<sub>B</sub>* value is about 8.7. The absorption band and *K<sub>B</sub>* value would identify the substance as an aromatic amine, and it might be a substituted pyridine.

**Base Strength.**—These compounds are bases by virtue of their power to donate a share in the lone pair of electrons to an acid. Since the light absorption is due to an excitation of these electrons it was of interest to see if any correlation was to be observed between these properties. The base strength in aqueous solution is the most commonly measured property although the complications of hydration add to those of steric factors in making the situation far from simple.

Values of *pK<sub>B</sub>* obtained in this Laboratory and elsewhere are shown in Table V. The values given are thermodynamic constants except that, where the ionic strength is not recorded, they may be classical constants. There are many other measurements of pyridine with values ranging from 8.52 to 8.89 summarized in one of the references.<sup>18</sup> Piperidine also has been measured by others<sup>19</sup> but little work has been recorded on the other compounds.

(17) H. Ley and F. Volbert, *Ber.*, **59B**, 2119 (1926).

(18) E. B. Hughes, H. H. G. Jellinek and B. A. Ambrose, *J. Phys. Colloid Chem.*, **53**, 410 (1949).

(19) W. F. K. Wynne-Jones and G. Salomen, *Trans. Faraday Soc.*, **34**, 1321 (1938). See also G. von Weisse and M. Levy, *J. chim. phys.*, **14**, 261 (1916); R. J. Bruehlmann and F. H. Verhoek, *THIS JOURNAL*, **70**, 1401 (1948); N. F. Hall and M. R. Sprinkle, *ibid.*, **54**, 3469 (1932).

TABLE V  
 BASE STRENGTH MEASUREMENTS

| Substance   | Method <sup>a</sup> | Temp.,<br>°C. | Ionic<br>strength<br>ap-<br>prox-<br>imate | pK <sub>B</sub> | Investigator                                |
|-------------|---------------------|---------------|--|-----------------|---|
| Pyridine    | s                   | 24.3          | 0.02                                       | 8.80            | Wieder, this lab.                           |
|             | s                   | 20.0          | .028                                       | 8.88            | Hughes, <i>et al.</i> <sup>12</sup>         |
|             | s                   | 25.3          | .01  | 8.84            | Herington <sup>20</sup>                     |
| Piperidine  | s                   | 24.3          |  | 2.97            | Corning, this lab.                          |
|             | s                   | 25.0          | 0.005                                      | 3.00            | Semenov, this lab.                          |
|             | p                   | 25.0          | 0  | 2.94            | Wynne-Jones,<br><i>et al.</i> <sup>13</sup> |
| Pyrrolidine | s                   | 25.6          | 0.005                                      | 3.02            | Semenov, this lab.                          |
|             | p                   | 25.0          | 0.005                                      | 2.99            | Buckley, this lab.                          |
|             | p                   |               |  | 2.89            | Craig and Hixon <sup>21</sup>               |

(20) E. F. G. Herington, *Disc. Faraday Soc.*, **9**, 26 (1950).(21) L. C. Craig and R. M. Hixon, *THIS JOURNAL*, **53**, 4367 (1931).

|            |   |      |      |      |                         |
|------------|---|------|------|------|-------------------------|
| Piperazine | p | 23.5 | 0.01 | 4.22 | Wieder, this lab.       |
|            |   |      |      | 8.49 |                         |
|            | p | 15.0 |      | 4.02 | Koltthoff <sup>22</sup> |
|            |   |      | 8.34 |      |                         |
|            |   | 25.0 |      | 4.19 | Bredig <sup>23</sup>    |

<sup>a</sup> s = spectrophotometric, p = potentiometric.

Pyrrolidine and piperidine are extremely strong bases while piperazine is not as strong even for the first ionization, showing that the second nitrogen atom has an inductive effect. Pyridine is a very weak base and pyrrole is not measurable in aqueous solution. No significant relation was found between the position of the absorption band and the base strength in aqueous solution.

(22) I. M. Koltthoff, *Biochem. Z.*, **162**, 289 (1925).(23) G. Bredig, *Z. physik. Chem.*, **13**, 312 (1894).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE, AND THE OREGON FOREST PRODUCTS LABORATORY]

## The Infrared Spectra of Lignin and Related Compounds. I. Characteristic Carbonyl and Hydroxyl Frequencies of Some Flavanones, Flavones, Chalcones and Acetophenones<sup>1</sup>

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The hydroxyl and ketone carbonyl infrared frequencies of a series of flavanones and related compounds have been measured. An *o*-hydroxyl group chelated to a carbonyl group effects a shift of 60 cm.<sup>-1</sup> to a longer wave length. Shifts to shorter or longer wave lengths were observed when electron-withdrawing or supplying constituents were introduced into ring positions conjugated with the carbonyl group. The effects of intramolecular and intermolecular hydrogen bonding upon the carbonyl frequency are shown and discussed.

Infrared spectroscopy has proved to be an especially useful tool in the field of lignin chemistry since it provides a rapid method of evaluating lignins isolated by different methods.<sup>2a-f</sup> Application of the infrared method toward the structural elucidation of lignin has been hindered, however, by the lack of sufficient data concerning certain functional group frequencies in solid organic compounds. This information is necessary, since lignin may be prepared only as a mull or a film because of its insolubility in the solvents ordinarily used in infrared analysis.

Examination of the infrared spectra of lignin and lignin derivatives prepared in this Laboratory indicates the presence of two bands, 1666-1668 cm.<sup>-1</sup> and 1705-1710 cm.<sup>-1</sup>, which presumably originate from conjugated aldehyde and ketone carbonyl groups, respectively. Other materials related to lignin, such as tannin and phlobaphene, also show bands assignable to carbonyl groups. It seemed to be advantageous, therefore, to study a series of known solid compounds that may be related to lignin and contain hydroxyl, methoxyl and carbonyl groups. The results from the study of the first series of these compounds are presented here.

(1) From the Ph.D. thesis of H. L. Hergert to be submitted to the graduate school of Oregon State College. This paper was presented at the Northwest Regional Meeting of the American Chemical Society at Corvallis, Oregon, June 20, 1952.

(2) (a) G. de Stevens and F. F. Nord, *THIS JOURNAL*, **73**, 4622 (1951); (b, c) S. F. Kudzin and F. F. Nord, *ibid.*, **73**, 690, 4619 (1951); (d) S. F. Kudzin, R. M. DeBaun and F. F. Nord, *ibid.*, **73**, 4615 (1951); (e) E. J. Jones, *Tappi*, **32**, 167 (1949); (f) K. Freudenberg, *et al.*, *Ber.*, **83**, 533 (1950).

### Experimental

**Spectra.**—The instrument used in this work is a model 12C Perkin-Elmer spectrometer and Brown recorder adapted to automatic, double-beam operation by the method of Savitsky and Halford.<sup>3</sup> Lithium fluoride optics were used in the 2500-4000 cm.<sup>-1</sup> region and sodium chloride in the 1550-1800 cm.<sup>-1</sup> region. Solid samples were milled in mineral oil (Nujol) or perfluorokerosene and run against a salt plate as a blank.

**Compounds.**—Benzalacetophenone (chalcone) and the hydroxy acetophenones were purchased from the Eastman Kodak Company. Purification was effected by recrystallization or fractional distillation, whichever was appropriate. Derivatives were prepared by known methods.

Flavanone was prepared by the method of Kostanecki and Szabranski.<sup>4</sup> The method of Kurth<sup>5</sup> was used to prepare 2,4-dihydroxyflavanone and its corresponding chalcone. Douglas fir bark cork<sup>6</sup> was used as a source of *d*-3,3',4',5',7-pentahydroxyflavanone. The pentaacetate derivative, m.p. 128-129° from methanol, was prepared by the acetic anhydride-pyridine method. The 3',4',7-trimethoxy and pentamethoxy derivatives of this flavanone were prepared by diazomethane and dimethyl sulfate methylation, respectively, by Mr. Peter Coad and will be described in detail in a subsequent publication. The pentahydroxyflavanone was converted to the corresponding flavone (quercetin) by treatment with aqueous sodium bisulfite.<sup>7</sup> Pentamethoxy- and 3,3',4',7-tetramethoxyquercetin were prepared by the method of Gomm and Nierenstein.<sup>8</sup> The method of Pew<sup>9</sup>

(3) A. Savitsky and R. S. Halford, *Rev. Sci. Instruments*, **21**, 203 (1950).(4) V. Kostanecki and Szabranski, *Ber.*, **37**, 2635 (1904).(5) E. F. Kurth, *THIS JOURNAL*, **61**, 861 (1939).(6) H. L. Hergert and E. F. Kurth, *Tappi*, **35**, 59 (1952).(7) E. F. Kurth and F. L. Chan, *J. Am. Oil Chem. Soc.*, **28**, 433 (1951).(8) A. S. Gomm and M. Nierenstein, *THIS JOURNAL*, **53**, 4408 (1931).(9) J. C. Pew, *ibid.*, **70**, 3031 (1948).