599. *Infra-red Spectroscopic Measurements of Substituted Pyrimidines. Part II. The Absorption Spectra of Di-, Tri-, and Tetra-substituted Pyrimidines.*

By I. A. Brownlie.

The infra-red absorption spectra of a number of solid di-, tri-, and tetra-substituted pyrimidines have been measured between 2 and 15 μ., and the spectrum of liquid pyrimidine has been measured over the same region. Differences of absorption in the 5—15 μ. region depend on the number and position of substituents in the pyrimidine ring, as well as on the nature of these substituents, whereas the results in the 3 μ. region depend principally on the type of the substituents. The majority of the absorption bands in the 3 μ. region have been identified, and a number of frequencies in the 5—15 μ. region characteristic of the di-, tri-, and tetra-substituted pyrimidines, respectively, have been observed.

In Part I of this series (Brownlie, Sutherland, and Todd, *J.*, 1948, 2265) it was shown that the presence of hydrogen bonding in certain acetylated 4-D-glycosidaminopyrimidines could be clearly detected by infra-red spectroscopy. In every case where chemical behaviour had required the hypothesis of hydrogen bonding, the infra-red evidence supported this hypothesis, and conversely when the chemical evidence was against chelation, the infra-red evidence clearly showed the absence of hydrogen bonding.

This investigation, however, formed part of a larger programme of work, involving the examination of the vibrational spectra, from 2 to 15 μ., of pyrimidine, and of substituted pyrimidines containing two, three, and four substituents. The 25 compounds selected for examination included those with the following substituents: NH_2, NHMe, OH, SH, SMe, Me, NO, NHAc, NH–D-glucose, NH–D-xylose, NH–triacetyl-D-xylose. Unfortunately, no suitable monosubstituted pyrimidines were available. The object of the investigation was to identify the

vibrational frequencies corresponding to each substituent, whether they be stretching vibrations or associated bending oscillations; to determine if these were dependent on the total number of substituents, and on their position in the nucleus; and lastly, to determine if possible any relationship between the characteristic skeletal vibration frequencies of each substituted pyrimidine, and the number and position of the substituents.

Experimental.

Since most of the substituted pyrimidines are soluble only in solvents which absorb strongly in the region 2—15 μ. (5000—667 cm.$^{-1}$), they were examined as a capillary layer, between rock-salt plates, of a fine suspension of the substance in " Nujol." A sample of pyrimidine was examined in the liquid state at cell thicknesses of 0·06 and 0·025 mm. These measurements were made on a double-beam spectrometer (Sutherland and Thompson, *Trans. Faraday Soc.*, 1945, **41**, 174) fitted with a 30° rock-salt prism of the Littrow type, and a Hilger Schwarz vacuum thermopile. The compounds were further examined in the range 2—6 μ. on a special spectrometer of very high resolving power (cf. Sutherland, Blackwell, and Fellgett, *Nature*, 1946, **158**, 873) fitted with a lithium fluoride prism.

Results and Discussion.—The only previous report of the spectrum of pyrimidine (Barnes, Gore, Liddel, and Williams, " Infra-Red Spectroscopy," p. 97, New York, 1944) gives a band at 1775 cm.$^{-1}$, which is not shown by our sample and is probably due to impurity. As the similarity in the infra-red spectra of benzene and pyridine has often been observed, the absorption frequencies (in cm.$^{-1}$) of benzene and pyrimidine are compared in Table I, and are seen to be very similar. It would be expected that the replacement of each of two CH groups in benzene by a nitrogen atom would not appreciably alter the vibrations other than those of the hydrogen atoms. Kline and Turkevitch (*J. Chem. Physics*, 1944, **12**, 300) have shown that the ring vibrations of pyridine parallel those of benzene and can be readily located, and that the hydrogen vibrations of pyridine show considerable divergence from those of benzene and can only be tentatively assigned; in general, transition from benzene to pyridine causes a displacement of the hydrogen frequencies towards lower frequencies. The C–H bending frequencies in pyrimidine may be tentatively assigned to the 1230 cm^{-1}. and 820 cm^{-1}. absorption bands, in-plane and out-of-plane, respectively. It will be observed that in Table I there is no pyrimidine frequency corresponding to the benzene C–H aromatic valency vibration at 3065 cm.$^{-1}$, but it is probable that this frequency was obscured by the very strong band at 3400 cm.$^{-1}$.* In contrast to the resonance formula of benzene which has three carbon–carbon double bonds, pyrimidine has two carbon–nitrogen double bonds, and one carbon–carbon double bond, so that in addition to C=C valency vibrations we might expect C=N valency vibrations. There are, in fact, two strong absorption frequencies observed, *viz.*, those at 1570 and 1650 cm.$^{-1}$, which are probably due, respectively, to these double-bond valency vibrations. Although it might be argued that resonance would make unlikely the possibility of distinguishing between C=C and C=N valency vibrations, yet for the sake of comparison with the substituted pyrimidines these two frequencies will be referred to as if they are due to those respective vibrations. Another frequency in pyrimidine, at 1400 cm.$^{-1}$, is also shown by the substituted pyrimidines, as noted later.

Table I.*

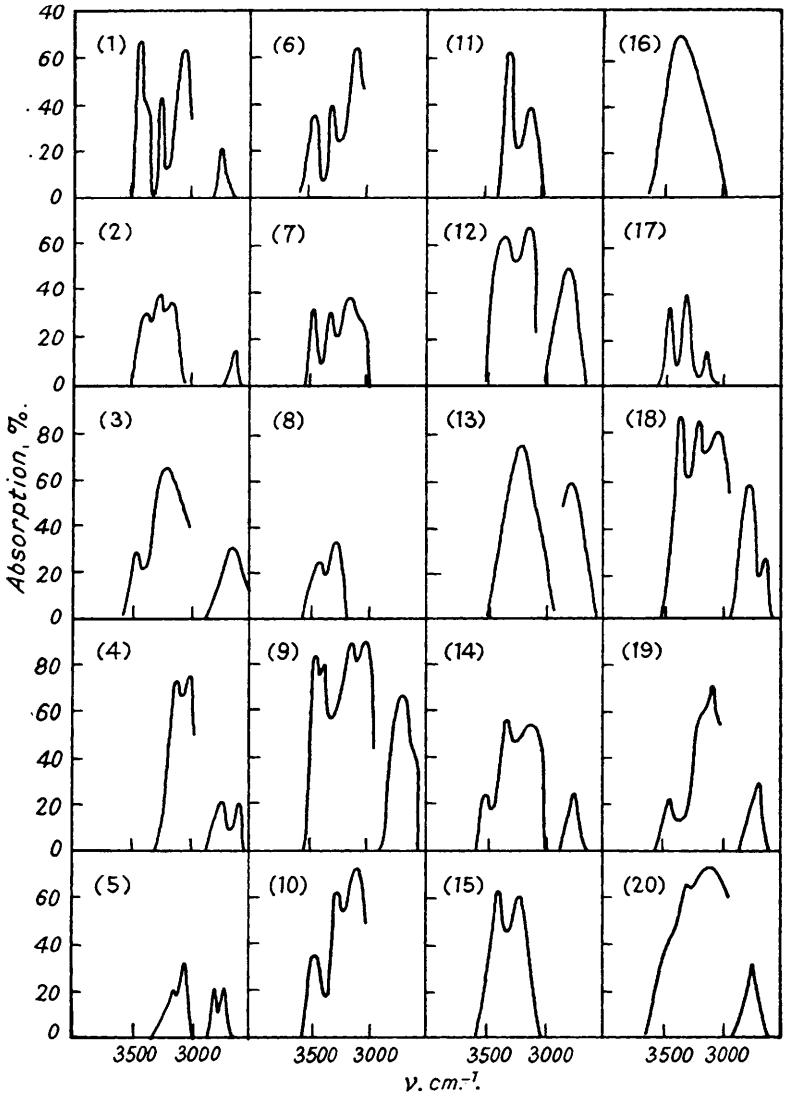
Benzene	849	1033	—	1150	1175	1247	1393	1478	1530	1588
Pyrimidine	825	1000	1080	1140	1165	1230	1400	1465	—	1570
Benzene	1650	1822	1965	—	2600	—	2880	2950	3065	—
Pyrimidine	1650	—	1940	2520	2620	2710	2880	—	—	3400

* The data for liquid benzene are due to Halford and Schaeffer (*J. Chem. Physics*, 1946, **14**, 141).

The graphical results for di-, tri-, and tetra-substituted pyrimidines in the 3 μ. region are shown in Figs. 1 and 2, and in Tables II and III are listed the absorption frequencies for each compound. Each of the absorption frequencies has been assigned to a valency vibration of one of the substituents, or of the C–H vibration in the pyrimidine ring, when the number of substituents is less than four. It will be seen in Figs. 1 and 2 that in four molecules only one band either at 2650 cm.$^{-1}$ or at 2750 cm.$^{-1}$ is unaccounted for in the tables, and it is probable that this is an overtone. The C–H valency vibration of CH_3 or CH_3S substituents occurs at 2750 cm.$^{-1}$, but where it is not observed it is probably obscured by the strong " Nujol " band at 2900 cm.$^{-1}$. As the compounds, except pyrimidine itself, were all examined in the solid state, it is to be expected that the N–H (both in NHAc and NH_2) and O–H valency vibrations should be

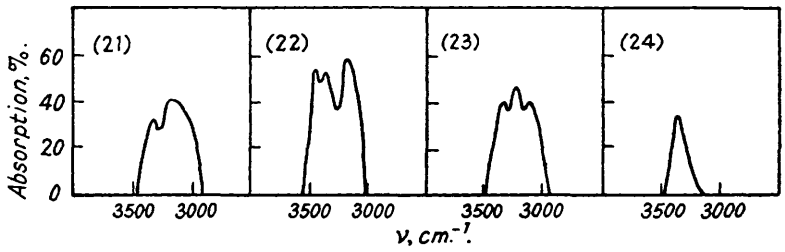
* Further investigations on the pyrimidine spectrum with special reference to the band at 3400 cm.$^{-1}$ are in course of publication (Sutherland and Skogh, private communication).

FIG. 1.



Curve No.	*Compound.*
1	4 : 6-*Diaminopyrimidine.*
2	4-*Amino*-6-D-*glucosidaminopyrimidine.*
3	4-*Amino*-6-D-*xylosidaminopyrimidine.*
4	4-*Hydroxy*-2-*mercapto*-6-*methylpyrimidine.*
5	4-*Hydroxy*-2-*methylthio*-6-*methylpyrimidine.*
6	4 : 6-*Diamino*-2-*methylpyrimidine.*
7	4 : 6-*Diamino*-2-*methylthiopyrimidine.*
8	4 : 6-*Diamino*-2-*mercaptopyrimidine.*
9	4 : 6-*Diamino*-2-*hydroxypyrimidine.*
10	6-*Amino*-4-*methylamino*-2-*methylpyrimidine.*
11	4-*Methylamino*-2-*methylthio*-6-*methylpyrimidine.*
12	6-*Amino*-4-*hydroxy*-2-*methylpyrimidine.*
13	6-*Amino*-4-*hydroxy*-2-*methylthiopyrimidine.*
14	6-*Amino*-4-D-*xylosidamino*-2-*methylthiopyrimidine.*
15	6-*Amino*-4-*acetamido*-2-*methylthiopyrimidine.*
16	4-D-*Xylosidamino*-6-*acetamido*-2-*methylthiopyrimidine.*
17	4-(*Triacetyl*-D-*xylosidamino*)-6-*acetamido*-2-*methylthiopyrimidine.*
18	4-*Hydroxy*-5-*acetamido*-2 : 6-*dimethylpyrimidine.*
19	5-*Amino*-4-*mercapto*-2 : 6-*dihydropyrimidine.*
20	5-*Nitroso*-4 : 6-*diamino*-2-*methylpyrimidine.*

FIG. 2.



Curve No.	*Compound.*
21	5-*Nitroso*-4 : 6-*diamino*-2-*thiopyrimidine.*
22	5-*Nitroso*-6-*amino*-4-*methylamino*-2-*methylthiopyrimidine.*
23	5-*Nitroso*-6-*amino*-4-D-*xylosidamino*-2-*methylthiopyrimidine.*
24	5-*Nitroso*-6-*amino*-4-(*triacetyl*-D-*xylosidamino*)-2-*methylthiopyrimidine.*

TABLE II.

Stretching vibrations in 3 μ. *region* (*cm.*$^{-1}$) *for* 4 : 6-*diaminopyrimidines.*

No.	Substituent in position 2.	C–H.	N–H.	O–H.	No.	Substituent in position 2.	C–H.	N–H.	O–H.
1	(H)	3050	3250 3450	—	4	OH	3050	3350 3450	3150
2	Me	3080	3300 3450	—	5	SH	—	3300 3450	—
3	SMe	3100	3300 3450	—	6	Me †	3080	3250 3450	—

† For 4-amino-6-methylamino-2-methylpyrimidine.

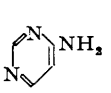
TABLE III.

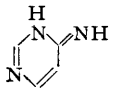
Stretching vibrations in 3 μ. *region* (*cm.*$^{-1}$).

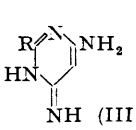
No.	Substituent in position : 2.	4.	5.	6.	C–H.	N–H.	O–H.	O–H (sugar).	C–H (Me or SMe).	S–H.	NHAc.
1	Me	OH	—	NH_2	In O–H	3350	3150	—	2800	—	—
2	SMe	OH	—	NH_2	—	3250	—	—	2800	—	—
3	SMe	Me	—	OH	3050	—	3150	—	2750	2700	—
4	SMe	Me	—	NHMe	3100	3250	—	—	—	—	—
5	SH	Me	—	OH	3050	—	3100	—	2750	2620	—
6	—	NH_2	—	NH–D-glucose	In O–H	3300 3450	—	3200	—	—	—
7	—	NH_2	—	NH–D-xylose	—	3500	—	3250	—	—	—
8	SMe	NH_2	—	NH–D-xylose	In O–H	3350 3450	—	3200	2750	—	—
9	Me	NH_2	—	NH–D-xylose	In O–H	3300	—	3200	—	—	—
10	SMe	NHAc	—	NH–D-xylose	One strong band at 3350 cm.$^{-1}$.						
11	SMe	NHAc	—	NH–(triacetyl-D-xylose)	3100	—	—	—	—	—	3320 3460
12	SMe	NHAc	—	NH_2	—	3200 3350	—	—	—	—	See N–H
13	Me	Me	NHAc	OH	—	—	3050	—	2800	—	3250 3400
14	OH	SH	NH_2	OH	—	3150 3450	3050	—	—	2650	—
15	SH	NH_2	NO	NH_2	—	3350	—	—	—	—	—
16	Me	NH_2	NO	NH_2	—	3250 3400	—	—	2750	—	—
17	SMe	NHMe	NO	NH_2	—	3250 3350	—	—	—	—	—
18	SMe	NH–D-xylose	NO	NH_2	—	3450	—	3250 3300	—	—	—
19	SMe	NH–(triacetyl-D-xylose)	NO	NH_2	—	3370	—	—	—	—	—

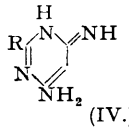
displaced to lower frequencies by association. It has been found that they do, in fact, appear at frequencies lower than those shown by non-associated compounds. In particular, hydroxyl groups directly substituted in the pyrimidine ring give rise to absorption bands at 3150 cm.$^{-1}$, and the O–H absorption from NH–D-xylose or NH–D-glucose substituents lies at approximately 3200—3350 cm.$^{-1}$. In both cases the hydroxyl groups are strongly bonded. It will be noted in Table III that the strong absorption bands of compound No. 10 at 3350 cm.$^{-1}$ and of compound No. 18 at 3250—3300 cm.$^{-1}$, which are both due to the three hydroxyl groups in the D-xylosidamino-substituent, are completely removed by triacetylation, as shown by compounds No. 11 and 19.

In the substituted aminopyrimidines we have the possibility of tautomerism as, *e.g.*, (I) $\rightleftharpoons$ (II) in 2-aminopyrimidine. We have not examined any monosubstituted pyrimidines, but the diaminopyrimidines are interesting in this connection. In 4 : 6-diaminopyrimidines in which the substituent at position 2 is H, alkyl, methylthio-, or any group other than those (OH, NH, or SH) capable of prototropic change, the tautomeric possibilities indicate that one of the amino-groups is unaffected and should show true amino-character, *e.g.*, as in (III or (IV). This is


(I.)


(II.)

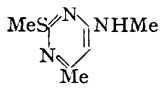

(III.)

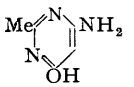

(IV.)

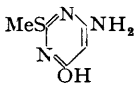
supported by the fact that the two N–H frequencies at ~3250 and 3450 cm.$^{-1}$ are shown by all the diaminopyrimidines (Table II, 1—6) with the exception of one case where a nitroso-group is present in the 5-position. These two N–H frequencies, whose relative intensities will be seen to vary with the type of substituent in the 2-position, may be compared with those shown by aniline at 3448 and 3368 cm.$^{-1}$.

With one exception the C–H valency vibration at 3050—3100 cm.$^{-1}$ is also clearly shown by this group of compounds in Table II.

The monoamino-compounds (V), (VI), and (VII) show only one N–H frequency. This fact agrees with the structure (V), which contains a methylamino-substituent, and therefore should exhibit only one N–H stretching frequency, as there is no other amino-substituent in the molecule. In (VI) and (VII) one would normally expect two N–H frequencies, but the


(V; 3250 cm.$^{-1}$)


(VI; 3350 cm.$^{-1}$)


(VIII; ~3250 cm.$^{-1}$)

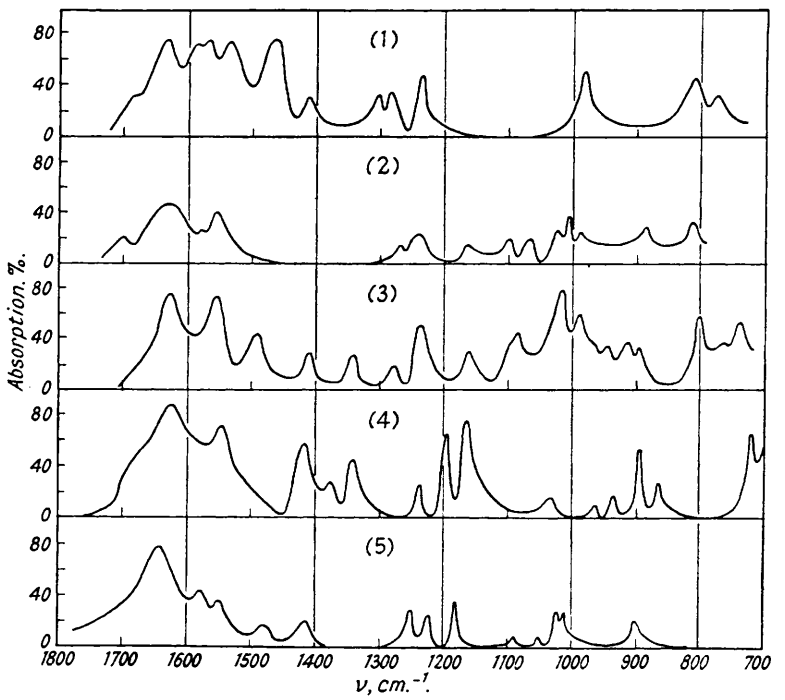
results could indicate that these compounds are largely in the tautomeric imino-form and therefore show only one N–H frequency. The amino- and hydroxyl groups are so situated in the molecule that their electromeric displacements are additive, giving greatly increased electron availability at the nitrogen atoms in the ring and at the 5-position, thus facilitating tautomeric change.

Compounds containing the acetamido-group give either one or two absorption bands at 3250—3460 cm.$^{-1}$ approximately, which may be due to associated and non-associated N–H bands from the NHAc groups. In the examples of acetamido-substitution available, three have the acetamido-group in the 4-position, and one has it in the 5-position. With those in the 4-position it would be expected that only intermolecular association would occur between the acetamido-carbonyl group and an NH (amino) or NH (acetamido) group to give an N–H $\cdots$ O bridge. With an acetamido-group in the 5-position, however, both intra- and inter-molecular association are possible between the acetamido-carbonyl group and the adjacent hydroxyl group to give a >C=O $\cdots$ H bridge. It will be noted that the O–H stretching frequency in this case is at the very low frequency of 3050 cm.$^{-1}$, which is evidence of considerable association. The non-associated N–H stretching vibration would be expected at ~3400 cm.$^{-1}$, whereas the presence of hydrogen bonding with formation of N–H $\cdots$ O or >C=O $\cdots$ H bridges would be expected to give rise to a lowered frequency, in this case to ~3250 cm.$^{-1}$. Where an amino-group is present in the molecule in addition to an acetamido-group, it is not possible to decide which absorption frequencies are characteristic of the respective groups, as they may be present as one broad band.

It will be observed from Figs. 1 and 2 that compounds having a nitroso-substituent in the

5-position exhibit either one or two bands in the region 3050—3150 cm.$^{-1}$. This is not readily characterized as being due to a stretching vibration of any of the substituents, and cannot be a C–H stretching vibration frequency since the molecule in each case is fully substituted. The effect, however, may be explained as arising from association involving the nitroso-group either as an intramolecular association involving an adjacent amino-group, or as an intermolecular association again with an amino-group. The resultant N–H · · · O bridge would give rise to such a displaced N–H frequency, particularly in the case of an intermolecular association, as the shift to 3050 or 3150 cm.$^{-1}$ is rather large for intramolecular association. This explanation cannot, for the time being, be proved conclusively, owing to the small range of nitroso-pyrimidines available, and the fact that there is more than one amino-group in the molecule complicates the interpretation.

FIG. 3.



Curve No.	*Compound.*
1	4 : 6-*Diaminopyrimidine.*
2	4-*Amino*-6-D-*glycosidaminopyrimidine.*
3	4-*Amino*-6-D-*xylosidaminopyrimidine.*
4	4-*Hydroxy*-2-*thio*-6-*methylpyrimidine.*
5	4-*Hydroxy*-2-*methylthio*-6-*methylpyrimidine.*

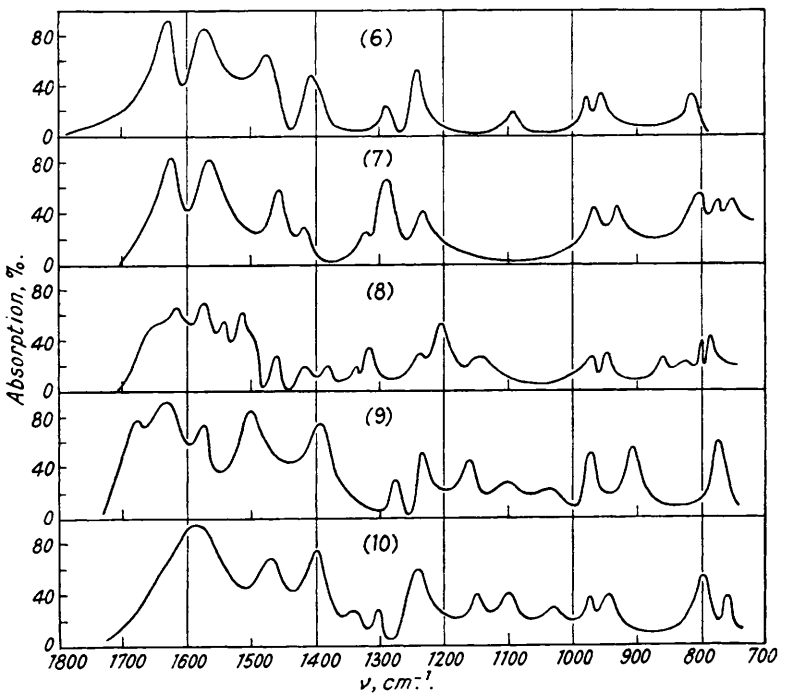
In Figs. 3—7 are shown the absorption curves, from 5 to 15 μ., of all the substituted pyrimidines examined. After careful comparison of the individual spectra with each other and with that of pyrimidine, it was found that there were present three characteristic frequencies, which appeared to be only slightly modified in value, as the number of substituents changed. Two of these, shown in Table IV, at 1620—1640 and 1560—1580 cm.$^{-1}$ have already been characterized in pyrimidine as the C=N stretching vibration, and the C=C stretching vibration respectively, and it will be remembered that in this connection the effects of resonance were mentioned. It is noteworthy that in the trisubstituted pyrimidines, 4-methylamino-2-methylthio-6-methylpyrimidine (Fig. 5, No. 11) and 6-amino-4-methylamino-2-methylpyrimidine (Fig. 4, No. 10), these double-bond vibrations occur as one very strong band at ~1590 cm.$^{-1}$, which in the former case has some signs of structure at 1575 cm.$^{-1}$. It is possible that the resonance in these compounds is higher than in the other substituted pyrimidines showing the double-bond stretching vibrations at 1620 and 1580 cm.$^{-1}$, and that this accounts for the lowered value of the double-bond frequencies.

TABLE IV.

Disubstituted pyrimidines, cm.$^{-1}$.	Trisubstituted pyrimidines, cm.$^{-1}$.	Tetrasubstituted pyrimidines, cm.$^{-1}$.	Remarks.
1620—1640	1610—1640	1625—1635	C=N stretching vibration
1560—1580	1580	1555—1575	C=C stretching vibration
1400—1420	1400—1420	1400—1420	Skeletal vibrations
1280—1295	1300	1295—1310	
1245	1250	—	C-H in-plane deformation
—	1160	1175	Present when NHMe present
1000	960—980	960—980	C-NH_2 bending vibration
—	—	1010—1020	Skeletal vibration
825	810—820	—	C-H out-of-plane deformation
—	—	775—795	Skeletal vibration

The band at 1400–1420 cm.$^{-1}$ shown by di-, tri-, and tetra-substituted pyrimidines is also present in pyrimidine, and appears to be a skeletal vibration of the pyrimidine nucleus. The 1280—1310 cm.$^{-1}$ vibration frequency is not shown by pyrimidine, but is shown by the three types of substituted pyrimidines and may be classed as a skeletal vibration of the substituted pyrimidine nucleus. The frequencies at 1010—1020 and 775—795 cm.$^{-1}$ present in tetra-substituted pyrimidines similarly appear to be skeletal vibrations characteristic of the tetra-substituted nucleus.

FIG. 4.



Curve No.	*Compound.*
6	4 : 6-*Diamino-2-methylpyrimidine.*
7	4 : 6-*Diamino-2-methylthiopyrimidine.*
8	4 : 6-*Diamino-2-thiopyrimidine.*
9	4 : 6-*Diamino-2-hydroxypyrimidine.*
10	6-*Amino-4-methylamino-2-methylpyrimidine.*

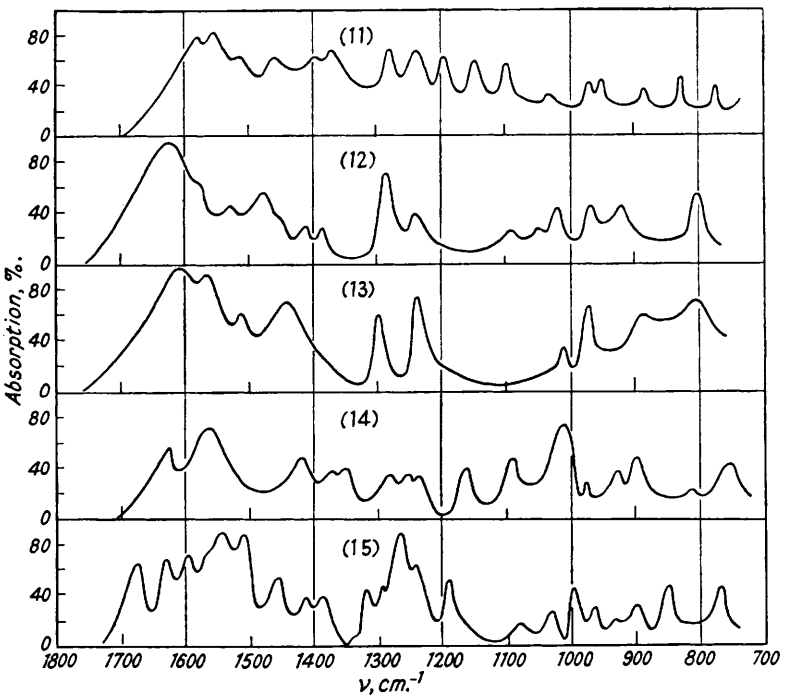
As the maximum number of substituents in the pyrimidine nucleus is four, it is evident that this class will not show any vibrations characteristic of the C–H stretching or deformation frequencies. This has already been demonstrated in the 3 μ. region. Comparison of tetra-substituted pyrimidines with di- and tri-substituted pyrimidines, and pyrimidine itself, reveals the frequencies at 1250 and 810—825 cm.$^{-1}$, which, especially as they are not present in the

tetrasubstituted pyrimidines, may be the C–H deformation frequencies, in-plane and out-of-plane, respectively.

The majority of the substituted pyrimidines examined contain one or more amino-groups, and in the three classes of substituted pyrimidines a band appears at ~980 cm.$^{-1}$ which may be classified as a C–NH_2 bending vibration frequency. One other frequency, at 1160—1175 cm.$^{-1}$, has been found when the methylamino-substituent is present in the 4-position.

In the trisubstituted pyrimidines it has been found that the presence of a methyl or methylthio-group in the 2-position has generally been accompanied by the presence of an absorption frequency at 1450—1480 cm.$^{-1}$ (see Table V). Although in a few cases this band has been too weak to be observed, as it lies in the region of the " Nujol " bands, it has never been observed when an amino- or hydroxy-group was substituted in the 2-position. It is probable that this frequency is characteristic of the $-CH_3$ deformation vibration.

FIG. 5.



Curve No.	*Compound.*
11	4-*Methylamino*-2-*methylthio*-6-*methylpyrimidine.*
12	6-*Amino*-4-*hydroxy*-2-*methylpyrimidine.*
13	6-*Amino*-4-*hydroxy*-2-*methylthiopyrimidine.*
14	6-*Amino*-4-D-*xylosidamino*-2-*methylthiopyrimidine.*
15	6-*Amino*-4-*acetamido*-2-*methylthiopyrimidine.*

TABLE V.

Trisubstituted pyrimidines with a methyl or a methylthio-group in the 2-position.

Substituent in position : 2.	4.	6.	Vibration frequency, cm.$^{-1}$.	Substituent in position : 2.	4.	6.	Vibration frequency, cm.$^{-1}$.
Me	NH_2	NH_2	1480	SMe	Me	NHMe	1465
Me	OH	NH_2	1480	SMe	OH	NH_2	1450
Me	NH_2	NHMe	1475	SMe	NHAc	NH_2	1460
SMe	Me	OH	1480	SMe	NH_2	NH_2	1465

From Table VI it will be seen that, in compounds containing the acetamido-group, two characteristic frequencies appear in the region 1600—1700 cm.$^{-1}$. The longer of these two can confidently be assigned to the C=O stretching frequency of the acetamido-group, which, as we have seen from evidence in the 3 μ. region, is involved in association. The range in the

TABLE VI.

Characteristic frequencies (cm.$^{-1}$) for compounds containing the acetamido-groups.

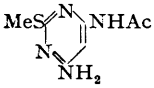
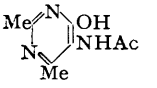
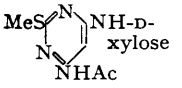
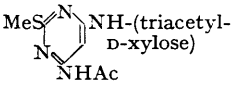
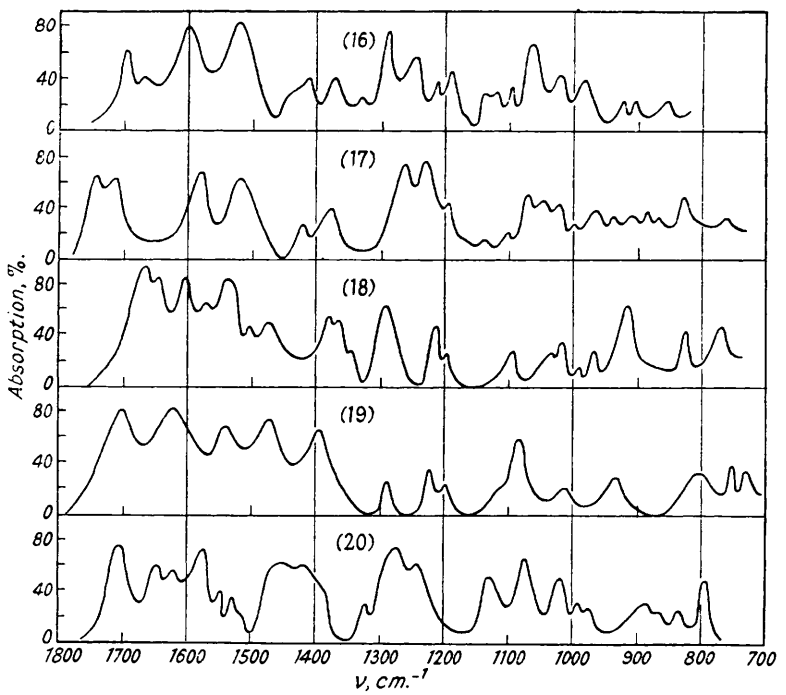
				
>C=O stretching frequency of triacetyl-D-xylose				
(*a*) Non-associated	—	—	—	1745
(*b*) Associated (cf. Part I, *loc. cit.*)	—	—	—	1710
>C=O stretching frequencies : acetamido-	1680	1670	1695	—
	1635	1650	1665	—
N–H bending frequency : acetamido-	1515	1510	1520	1520
Single bond stretching frequencies : acetamido-	1275	1295	1290	1270
	1200	1220	1215	1200

FIG. 6.



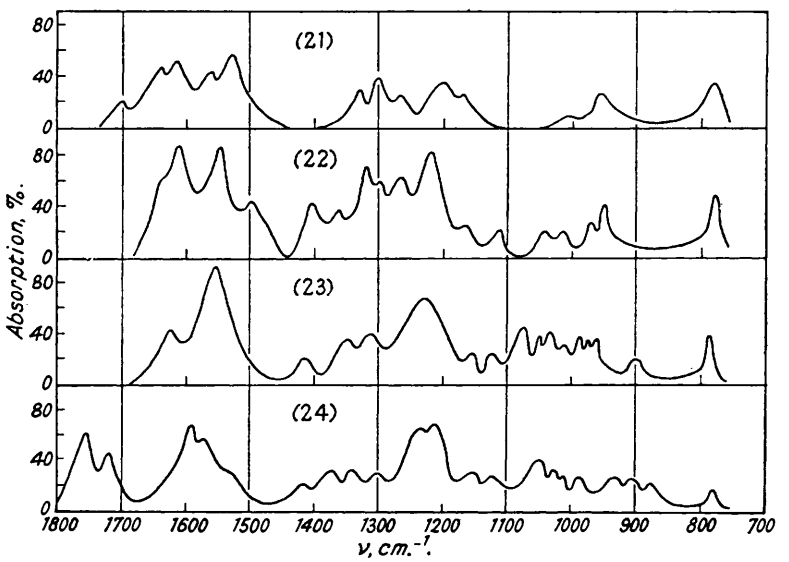
Curve No.	*Compound.*
16	4-D-*Xylosidamino*-6-*acetamido*-2-*methylthiopyrimidine.*
17	4-(*Triacetyl*-D-*xylosidamino*)-6-*acetamido*-2-*methylthiopyrimidine.*
18	4-*Hydroxy*-5-*acetamido*-2 : 6-*dimethylpyrimidine.*
19	5-*Amino*-2 : 6-*dihydroxy*-4-*thiopyrimidine.*
20	4 : 6-*Diamino*-5-*nitroso*-2-*methylpyrimidine.*

absolute value of its position can be ascribed to the varying degrees of association. It will be noted that the compound showing the lowest value of the longer frequency, *i.e.*, 1670 cm.$^{-1}$, is that containing the acetamido-group in the 4-position. This compound, as we have seen from evidence in the 3 μ. region, might be expected to have a higher degree of association than the others, and would have the C=O stretching frequency shifted to a lower value than the others. The band at 1635—1665 cm.$^{-1}$ is more difficult of explanation, but it will be noted from the absorption curves, that, in each of the acetamido-compounds, the C=N stretching frequency is moved from its normal position to ~1600 cm.$^{-1}$. This could be due to the fact that the C=O

frequency may be split by resonance with the double bond frequency of the pyrimidine nucleus, the C=N frequency being moved in consequence of this increased resonance to shorter frequencies. In the triacetylated compounds, where there is association within the NH–(triacetyl-D-xylose) group (Part I, *loc. cit.*), the acetamido-carbonyl frequency is obscured by the acetyl carbonyl frequencies, but, in this case also, the C=N and C=C stretching vibrations fall at lower frequencies. The band at 1510—1520 cm.$^{-1}$, again present only when there is an acetamido-substituent, may be classed as the N–H bending frequency of that group.

The region 1200—1300 cm.$^{-1}$ is interesting when the acetamido-group is present, for in all cases strong bands are present at 1200—1220 and 1270—1295 cm.$^{-1}$. These may be due to single-bond valency vibrations of the acetamido-group. Triacetylation of 4-D-xylosidamino-6-acetamido-2-methylthiopyrimidine gives rise to a strong band at 1235 cm.$^{-1}$, and a similar band at 1220 cm.$^{-1}$ is found in the triacetyl derivative of 5-nitroso-6-amino-4-D-xylosidamino-2-methylthiopyrimidine. This new band shown in the triacetyl compounds is probably due to the >C–O– valency vibration of the acetyl groups.

FIG. 7.



Curve No.	*Compound.*
21	5-*Nitroso*-4 : 6-*diamino*-2-*thiopyrimidine*.
22	5-*Nitroso*-6-*amino*-4-*methylamino*-2-*methylthiopyrimidine*.
23	5-*Nitroso*-6-*amino*-4-D-*xylosidamino*-2-*methylthiopyrimidine*.
24	5-*Nitroso*-6-*amino*-4-(*triacetyl*-D-*xylosidamino*)-2-*methylthiopyrimidine*.

The only remaining substituent to be considered, *viz.*, the nitroso-group, has also been found to show a characteristic absorption frequency. In 5-nitroso-4 : 6-diamino-2-methylpyrimidine (Fig. 6, No. 20), 5-nitroso-4 : 6-diamino-2-mercaptopyrimidine (Fig. 7, No. 21), and 5-nitroso-6-amino-4-methylamino-2-methylthiopyrimidine (Fig. 7, No. 22), absorption bands at 1650, 1645, and 1640 cm.$^{-1}$, respectively, may be identified as the N=O stretching vibration frequency. In each of these cases it can be distinguished from the C=N stretching frequency at 1615—1620 cm.$^{-1}$, although in the 4-methylamino-compound the N=O frequency is not clearly resolved, but appears as a shoulder on the 1625 cm.$^{-1}$ band. In 5-nitroso-6-amino-4-D-xylosidamino-2-methylthiopyrimidine and the corresponding triacetyl compound (Fig. 7, No. 23), the N=O frequency cannot be distinguished, and indeed, in the triacetyl compound, the C=N stretching vibration appears to be shifted from its usual position to 1590 cm.$^{-1}$. This band at 1590 cm.$^{-1}$, in which the 1575 cm.$^{-1}$ C=C stretching vibration can be distinguished, is very broad, and it may be that a study of this region under slightly higher resolving power would reveal the N=O stretching frequency. It will be remembered, however, that in the 3 μ. region there was evidence of intermolecular association which could be attributed to N–H···O bridges to the nitroso-group in position 5 of the molecule. As an appreciable degree of association in this manner

would have the effect of causing a shift in the position of the nitroso-stretching frequency towards the position of the double-bond stretching frequencies, there could arise an appreciable degree of interaction, which would render the detection of the nitroso-frequency very difficult.

In conclusion, it may be noted that, although the 3 μ. region can be almost completely characterized, it would appear that a study of many more substituted pyrimidines will be necessary before a number of other interesting correlations which suggest themselves can be fully explored. The 1200—1300 cm.$^{-1}$ region is particularly interesting in the pyrimidine series, especially for those compounds containing the nitroso- and acetamido-substituents. In the range of compounds already examined, the spectra shown are fully characteristic of each compound and can be readily distinguished. An interesting example of distinguishing between two closely related compounds may be shown by comparing the spectra of 4 : 6-diamino-2-methylpyrimidine (Fig. 4, No. 6) and 4 : 6-diamino-2-methylthiopyrimidine (Fig. 4, No. 7). There is a certain similarity in their spectra, particularly in the 800—1000 cm.$^{-1}$ region, and in the double-bond region of stretching frequencies from 1550 to 1650 cm.$^{-1}$. However, the reversal of intensity in the two bands in the 1200—1300 cm.$^{-1}$ region is, in itself, sufficient indication of the change in constitution provided by replacing a methyl by a methylthio-group.

This work was done in 1947 at the Department of Colloid Science, Cambridge. I wish to thank Professor G. B. B. M. Sutherland, F.R.S., who suggested the subject and provided the experimental facilities, Professor A. R. Todd, F.R.S., who provided samples of all the pyrimidine compounds examined, and the Ramsay Memorial Trust for the award of a Ramsay Fellowship during the tenure of which the work, described here and in Part I, was done.

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