Pteridine Studies. Part VI. The Ultraviolet and Infrared Absorption Spectra of the Monosubstituted Pteridines.*

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The absorption spectra of a number of monosubstituted pteridines have been measured in the ultraviolet and the visible region, between 200 and 500 mμ, and in the infrared between 4000 and 400 cm.$^{-1}$. A band due to an $n \longrightarrow \pi$ transition has been identified in the ultraviolet spectrum of pteridine, the effect of substituents upon that band indicating that the electron involved in that transition is located upon the 8-nitrogen atom. Various infrared bands of pteridine have been assigned to particular vibrational modes by comparisons between the spectra of the substituted pteridines.

Ultraviolet Spectra.—Pteridine, 1 : 3 : 5 : 8-tetra-azanaphthalene, possesses a π-electron structure similar to that of naphthalene, though some localization of the π-electrons may be expected in the former owing to the high proportion of doubly-bound nitrogen. Accordingly, electronic transitions between the π-electron orbitals, and the ultraviolet absorption bands arising from such transitions, should display similarities due to the structural resemblance and differences due to the partial localization of π-electrons on the nitrogen atoms and the presence of non-bonding σ-electrons on those atoms. It is found that naphthalene, pteridine, and the monoazanaphthalenes (Friedel and Orchin, " Ultraviolet Spectra of Aromatic Compounds," Wiley and Sons, New York, London, 1951, Nos. 195, 270, and 271) give rise to similar spectra in the region 200—320 mμ (Fig. 1), consisting, in general, of three bands.

The band of the longest wavelength in the ultraviolet spectrum of naphthalene, that at 320 mμ, is of low intensity ($\varepsilon_{max.}$ 250), being due to a symmetry-forbidden transition, or to an allowed transition of accidentally zero moment † (Craig, *Rev. Pure Appl. Chem.*, 1953, **3**, 207), but the introduction of one or more nitrogen atoms effects a perturbation which gives rise to a corresponding band of much greater intensity. The maximum extinction coefficient of this band is 7080 for pteridine (see Table 1), whilst the value calculated by adding vectorially the spectroscopic moments of the four nitrogen atoms, on the assumption that the corresponding band in naphthalene is due to a transition of accidentaly zero moment (Platt, *J. Chem. Phys.*, 1951, **19**, 263) is 10,100. The second band in the naphthalene spectrum is not so greatly changed in intensity by the introduction of nitrogen atoms but it is shifted from 280 mμ in naphthalene to 235 mμ in pteridine. The third band in the naphthalene spectrum is of high intensity (ε 100,000), and in the azanaphthalenes is reduced in height (for pteridine, ε 11,000).

Pteridine differs from naphthalene in possessing some unshared electrons, namely, those on nitrogen. One of these non-bonding electrons can undergo a transition to an unoccupied π-orbital of the rings, giving rise to a low-intensity band (ε 84) at 380 mμ which has no counterpart in the spectrum of naphthalene. This band may be identified as due to an $n \longrightarrow \pi$ transition by its low intensity, which arises from the lack of overlap between a σ(*n*)- and a π-orbital; by the fact that it shifts towards shorter wavelengths on

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* Part V, *J.*, 1954, 3832.

† Recent work (Sponer and Cooper, *J. Chem. Phys.*, 1955, **23**, 646) supports the latter view.

passage from a non-polar to a polar solvent, owing to interaction of the non-bonding electrons with the polar solvent molecules; and by the disappearance of the band in acid solution, the non-bonding electrons of the nitrogen being more firmly held in pteridine cation (Kasha, *Discuss. Faraday Soc.*, 1950, **9**, 14; McConnell, *J. Chem. Phys.*, 1952, **20**, 700; Platt, *J. Opt. Soc. Amer.*, 1953, **43**, 252). In aqueous solution interaction between the solvent and the pteridine molecule stabilises the ground state but not the excited state, because the ground- and the excited-state charge distributions do not overlap strongly, and, owing to the operation of the Franck–Condon principle, the energy of the $n \longrightarrow \pi$ transition is increased, shifting the band derived from that transition to shorter wavelengths. The band origin of the $n \longrightarrow \pi$ transition in pteridine, and the methyl-, chloro-, and methoxy-pteridines, undergoes a shift of some 1400 cm.$^{-1}$ on passage from *cyclo*hexane to aqueous solution, indicating that the strength of the hydrogen bonding between water and the pteridines examined is some 4 kcal./mole.

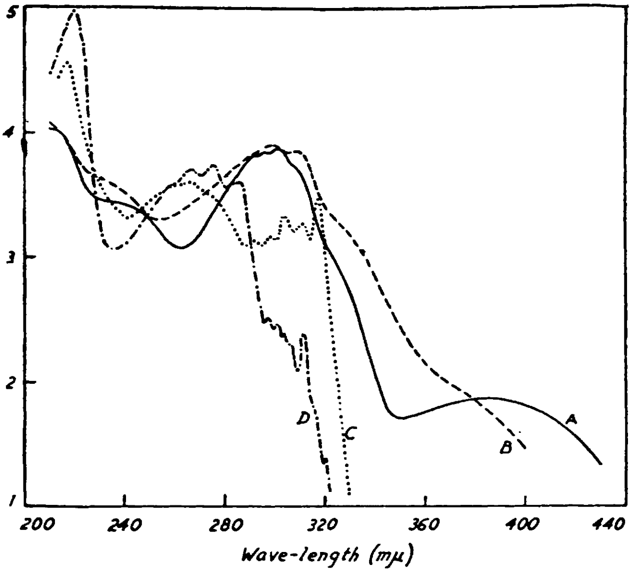


FIG. 1. *Ultraviolet absorption spectra of* (*A*) *pteridine in* cyclo*hexane,* (*B*) *pteridine* (*neutral molecule*), (*C*) iso*quinoline in* cyclo*hexane* (*Friedel and Orchin,* op. cit., *no.* 271), *and* (*D*) *naphthalene in* 95% *ethanol* (*ibid., no.* 195).

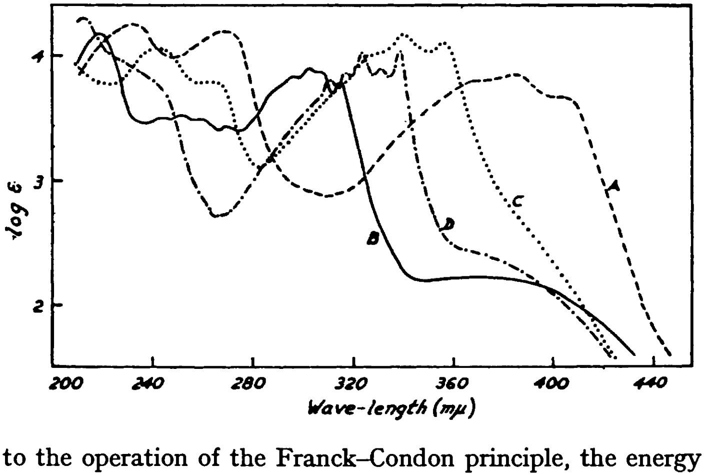


FIG. 2. *Ultraviolet absorption spectra of* (*A*) 6-*dimethylamino*-, (*B*) 4-*chloro*-, (*C*) 7-*methylthio*-, *and* (*D*) 2-*methoxy-pteridine, all in* cyclo*hexane.*

Substituents in the pteridine nucleus leave unchanged, or exert a hypsochromic effect upon, the position of the $n \longrightarrow \pi$ band of the pteridine spectrum, whilst they exert a marked bathochromic effect upon the $\pi \longrightarrow \pi$ bands (Fig. 2 and Table 1), so that the $n \longrightarrow \pi$ band is obscured by the long-wave $\pi \longrightarrow \pi$ band in the spectra of the methylthio- and dimethylamino-pteridines. The energy levels of the π-orbitals, filled or unfilled, tend

TABLE 1. *The ultraviolet and visible absorption bands* (mμ) *of pteridine and its derivatives. Values in italics refer to shoulders or inflexions, and values in braces refer to fine-structure peaks in a given band. The bands are classified according to their intensities.*

Substituent	Solvent *	pK_a in H_2O	$n \rightarrow \pi$ band λ	$n \rightarrow \pi$ band ε	1st $\pi \rightarrow \pi$ band λ	1st $\pi \rightarrow \pi$ band ε	2nd $\pi \rightarrow \pi$ band λ	2nd $\pi \rightarrow \pi$ band ε	3rd and 4th $\pi \rightarrow \pi$ bands λ	3rd and 4th $\pi \rightarrow \pi$ bands ε
Parent)	CH	—	395 387 380	78 84 84	*308* 301 296 *292*	5570 7490 6950 6340	*235*	2910	210	11,000
	H_2O, pH 6·10	—	*375*	79	309 298	7180 7730	*230*	4480	<210	>12,500
	H_2O, pH 1·70	4·12	—	—	300 286	8320 7640	—	—	<210	>9660
2-Methyl	CH	—	380	125	317 309 305	5640 7420 7380	*235*	3050	212	10,620
	H_2O, pH 6·90	—	*370*	112	317 305	7940 8320	*230*	4790	<215	>10,440
	H_2O, pH 2·70	4·87	—	—	301 285	8040 7730	248	3890	<215	>4120
4-Methyl	CH	—	394 386 378	90 95 94	*311* 304 300 294	5050 7075 7050 6275	270 248 243	2075 2675 2670	216 —	14,200 —
	H_2O, pH 6·05	—	349—353	163	312 300	7260 8420	*250*	2530	<220	>11,080
	H_2O, pH 1·0	2·90	—	—	306 280	9920 6120	—	—	<215	>14,120
7-Methyl	CH	—	375	108	*310* 302 298	6000 7720 7720	*239*	2750	212	9480
	H_2O, pH 6·90	—	*360*	170	310 298	8910 9550	*235*	3160	<220	>8240
	H_2O, pH 1·3	3·49	—	—	304 *285*	9770 7040	*255*	2350	<220	>3170
2-Chloro	CH	—	377	122	322 314 308 302	9250 8450 9220 7180	262 *243* *237*	1000 3900 5100	219	12,500
	H_2O, pH 7·0	—	*360*	277	319 307	8630 8990	258 *235*	2040 5010	<215	>17,040
4-Chloro	CH	—	371—373	165	315 307 303 296	6200 7500 7860 6740	270 260 252 244	2760 3140 3340 3160	220	15,000
	H_2O, pH 7·0	—	*350*	236	315 303	7640 8710	255 250	3160 3160	218	13,800
6-Chloro	CH	—	*365*	131	323 315 309 303	7980 7540 8800 6960	*240*	4600	<220	>15,220
	H_2O, pH 7·0	—	—	—	323 315 309 303	7950 7540 8790 6910	*235*	5620	<215	>15,140
7-Chloro	CH	—	354—355 344—345	236 237	316 308 303 297	7860 8480 9080 7600	*240*	3000	217	10,000

TABLE 1. (*Continued.*)

Substituent	Solvent [a]	pK_a in H_2O	n → π band λ	n → π band ε	1st π → π band λ	1st π → π band ε	2nd π → π band λ	2nd π → π band ε	3rd and 4th π → π bands λ	3rd and 4th π → π bands ε
	H_2O, pH 7·0	—	—	—	316 309 303	10,230 8870 9380	—	—	<215	>10,000
2-Methoxy	CH	—	*370*	250	339 331 324 318 311	10,640 7700 10,400 7080 6120	*238*	6720	213	19,700
	H_2O, pH 6·0	—	—	—	338 325	8080 8340	*240*	5500	<215	>17,620
	H_2O, pH 0	2·13	—	—	310—311	6380	*250*	5380	225	13,280
4-Methoxy	CH	—	389 381 374 367 360 353	143 212 261 287 286 268	319 313 307 301 295 291	6125 6025 8425 7425 6950 5675	273 263 255 *245*	2945 3025 2755 2165	226	21,700
	H_2O, pH 5·37	—	*350*	430	304	7730	257—260	2290	225	17,800
	H_2O, pH 1·0 [a]	1·04	—	—	302	9280	259	3400	218	8800
6-Methoxy	CH	—	*360*	292	331 323 316 309 303 297 291	9500 6780 9840 6500 6300 4320 3520	*240*	6300	216	20,700
	H_2O, pH 6·00	—	—	—	328 316 304	5620 6680 5700	*240*	5660	<215	>18,340
	H_2O, pH 1	3·60	—	—	288	12,380	—	—	<220	>14,720
7-Methoxy	CH	—	*340*	400	315 308 302 295 290 284 279	11,600 8700 11,680 8480 7800 5660 4500	254 *240*	1445 3940	214	18,300
	H_2O, pH 7·0	—	—	—	313 302	8910 9770	—	—	<215	>18,000
	H_2O, pH −0·8 [b]	1·64	—	—	298—300 275—277	6520 6240	—	—	220	21,360
2-Methylthio	CH	—	—	—	367 358	7720 7200	— —	— —	277 242	15,200 14,600
	H_2O, pH 5·50	—	—	—	360	7000	—	—	270 242	12,960 15,000
	H_2O, pH 0	2·2	—	—	*320*	6160	—	—	275 251	9840 20,800
4-Methylthio	CH	—	—	—	*364* *357* 348	7600 8040 9240	*295* 285	2580 2860	259 254 231	10,680 10,640 10,600
	H_2O, pH 4·90	—	—	—	353—354	8520	282—285	2760	254 238	8880 9000
	H_2O, pH 0	2·59	—	—	335	10,200	*290*	3840	232—233	9400
7-Methylthio	CH	—	—	—	356 341 331	12,200 14,360 10,240	263	6120	243	11,400

TABLE 1. (*Continued.*)

		pK_a in	$n \longrightarrow \pi$ band		1st $\pi \longrightarrow \pi$ band		2nd $\pi \longrightarrow \pi$ band		3rd and 4th $\pi \longrightarrow \pi$ bands	
Substituent	Solvent *	H_2O	λ	ε	λ	ε	λ	ε	λ	ε
	H_2O, pH 5·0	—	—	—	350	14,240	266	5560	240—241	9800
	H_2O, pH 0	2·50	—	—	343	10,840	278	4500	239	16,640
2-Dimethylamino	CH	—	—	—	434 441 390	4960 7280 6540	—	—	279 239	13,360 20,100
	H_2O, pH 7·1	—	—	—	410	6620	—	—	281—282 236	10,500 23,200
	H_2O, pH 1·0	3·03	355—360	450	305	7940	—	—	237	14,500
4-Dimethylamino	CH	—	—	—	*378* 362	5880 8160	290—294	1650	260 256 252 235	13,320 12,920 12,880 14,200
	H_2O, pH 7·0	—	—	—	362	8500	—	—	241	14,400
	H_2O, pH 2·0	4·33	—	—	345	12,420	—	—	239	13,900
6-Dimethylamino	CH	—	—	—	403 384 *369*	4570 6920 6040	—	—	269 232	15,640 17,400
	H_2O, pH 7·0	—	—	—	399	5540	*310*	2600	278 231	14,600 16,520
	H_2O pH 2·0	4·31	—	—	*322*	9400	—	—	300—298 222	15,200 21,280
7-Dimethylamino	CH	—	—	—	379 362 *351*	5760 9360 8480	—	—	269 240	9240 17,960
	H_2O, pH 5·0	—	—	—	362—366 366	11,200	—	—	279—280 240	9480 15,640
	H_2O, pH 0·5[a]	2·53	—	—	360—361	14,440	—	—	310—314 245	9160 8920
6 : 7-Dimethyl......	CH	—	370—372	109	314 301	8000 9760	*240*	3480	<215	>14,520
	H_2O, pH 6·0	—	*350*	234	314 301	9700 10,460	*235*	3440	<215	>13,660
	H_2O, pH 1·0	2·93	—	—	307	11,320	260	3460	<220	>1960
2 : 6 : 7-Trimethyl	CH	—	368—373	113	321 312 307 301	9120 8840 10,160 8040	*240*	3960	<220	>13,860
	H_2O, pH 6·50	—	*350*	324	320 307	10,720 11,220	*235*	*5480*	<220	>14,720
	H_2O, pH 1·0	3·76	—	—	307	11,860	255—256	4480	<220	>3000
2 : 4 : 6 : 7-Tetra-chloro	CH	—	*370*	405	343 337 327	11,520 9040 11,720	280	2160	238	19,780

* CH = *cyclo*hexane. [a] 5N-Sulphuric acid. [b] 4N-Sulphuric acid. [c] 0·33N-Hydrochloric acid.

to converge with increasing extranuclear conjugation, and, as expected, the bathochromic effect of substituents in the pteridine nucleus on the $\pi \longrightarrow \pi$ bands increases with the mesomeric effect of those substituents (Table 1), but the $\sigma(n)$-orbitals are localized and their binding energies are less affected by extranuclear conjugation. The hypsochromic effect of substituents on the $n \longrightarrow \pi$ band, which increases in the order Me < Cl < OMe, indicates that the unshared electrons of the nuclear nitrogen atoms are more firmly held in the substituted pteridines than in pteridine itself, because the π-orbital to which such an electron is excited is of lower energy in a substituted pteridine than in the parent molecule. In conformity with this indication it is found that the basic ionization constants of the known methyl- and methoxy-pteridines are lower than that of pteridine itself, except for 2-methylpteridine (Table 1). However, the base-weakening effect of a given substituent in the pteridine nucleus does not closely parallel its hypsochromic effect on the $n \longrightarrow \pi$ band of the pteridine spectrum, for the nitrogen atom from which the $n \longrightarrow \pi$ transition originates is not necessarily the basic centre of the pteridine molecule.

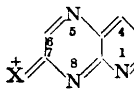
The most likely location of the non-bonding electron responsible for the $n \longrightarrow \pi$ band of the pteridine spectrum is the 8-nitrogen atom of the nucleus, because $n \longrightarrow \pi$ transitions are particularly sensitive to inductive effects (Goodman and Shull, *J. Chem. Phys.*, 1954, **22**, 1138), and substituents placed in the 7-position of pteridine exert a larger hypsochromic effect on the $n \longrightarrow \pi$ band of the pteridine spectrum, and enhance its intensity to a greater degree than when placed elsewhere (Table 1). However, the other nuclear nitrogen atoms contribute to the $n \longrightarrow \pi$ transition by interaction with the 8-nitrogen atom, since no $n \longrightarrow \pi$ band is observed in the spectrum of quinoline or *iso*quinoline. Interaction is more effective between 1 : 4- than between 1 : 3-aza-atoms, the $n \longrightarrow \pi$ band of pyrazine being of lower energy and more intense than that of pyrimidine (Halverson and Hirt, *J. Chem. Phys.*, 1951, **19**, 711); and of the two nitrogen atoms in the pyrazine ring of the pteridine nucleus, only that in the 8-position can compensate to some degree for the electron depletion caused by the inductive effect of a vicinal substituent by conjugation with the nitrogen atoms of the pyrimidine ring.

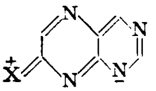
The effects of substituents on the π-electron spectra of pteridine and naphthalene show some similarities in regard to the bathochromic shifts induced by such substituents but not in respect of the intensity changes consequent upon substitution. A 2-substituent in naphthalene exerts a greater bathochromic effect upon the 320-mμ band of the naphthalene spectrum than a 1-substituent, whilst the reverse is true for the 280-mμ band (Friedel and Orchin, *op. cit.*, Nos. 196, 197, 236, 237, 250, 251, 264, and 265). In the spectrum of quinoline a substituent gives rise to similar relative bathochromic shifts when placed α or β to the bridge carbon atoms (Friedel and Orchin, *op. cit.*, Nos. 272—275); but for pteridine the parallel is not quite so close, for its 300-mμ band is moved towards longer wavelengths to approximately the same degree (Table 1) when a given substituent is placed in either the 4- or the 7-position, these being an α and a β position respectively. However, a substituent exerts the greatest bathochromic shift of the 235-mμ band of pteridine when it is in the 4-position, and a larger shift of the 300-mμ band when in the 2- or the 6-position than when in the 4-position.

In general, substituents in any given position of the pteridine nucleus exert a bathochromic effect on the 300-mμ band which increases in the order Me < Cl < OMe < SMe < NMe_2. These substituents follow the same order in regard to their bathochromic effect on the 260-mμ band of the benzene spectrum (Bowden and Braude, *J.*, 1952, 1068), and, so far as information is available, on the 320-mμ band of the naphthalene spectrum (Friedel and Orchin, *op. cit.*; Ferguson, *J.*, 1954, 304), a band which has been related by a spectroscopic sequence to the 260-mμ band of the benzene spectrum (Platt, *J. Chem. Phys.*, 1951, **19**, 101) and is taken in the present work as corresponding to the 300-mμ band of the pteridine spectrum. However, a given substituent produces a larger bathochromic shift of the pteridine spectrum than of the benzene and naphthalene spectra, the shift being very much larger when the substituent is introduced into the 2- or the 6-position.

Turning now from the consideration of wavelength shifts consequent upon substitution to changes of intensity, which are susceptible to more precise theoretical treatment in the case of cata-condensed hydrocarbons and their derivatives, it is found that there are considerable divergences between the effects of substituents on the spectra of naphthalene and pteridine. The intensity changes of the 260-mμ band of benzene and the 320-mμ band of naphthalene produced by a substituent may be accounted for quantitatively according to the theory of Sklar (*J. Chem. Phys.*, 1942, **10**, 135) and Forster (*Z. Naturforsch.*, 1947, **2**, a, 149), as developed by Platt (*J. Chem. Phys.*, 1951, **19**, 263) on the assumption that these bands are due to an allowed transition of accidentally zero moment. Applied to pteridine, this theory indicates that a given substituent should increase the intensity in the 300-mμ band of the pteridine spectrum, as a function of its position in the nucleus, in the following order: $4 < 0 < 7 < 2 = 6$. It is found, however, that a substituent in the pteridine nucleus always enhances the intensity of the 300-mμ band most when in the 7-position (average Δε 2280, for the substituents studied), and least, in general, when placed in the 6-position (average Δε 117), the effects of 2- and 4-substitution being about equal (average Δε 456 and 540 respectively).

The intensity changes in the 300-mμ band of the pteridine spectrum consequent upon monosubstitution may be explained more readily in terms of a transition to an excited state with a transannular polarity (Lewis and Calvin, *Chem. Rev.*, 1939, **25**, 273), than of one to an excited state with alternant polarities round the perimeter of the nulceus (Platt, *loc. cit.*). The localization of π-electrons on the nitrogen atoms of the pteridine nucleus, which has been calculated according to both the molecular-orbital and the valence-bond method (Albert, *Quart. Rev.*, 1952, **6**, 197), confers a dipole moment on the molecule, owing to its asymmetry, so that transannular polarized structures may be expected to contribute even to the ground state of the molecule. A 7-substituted pteridine can form two excited structures with transannular polarity (I*a* and I*b*), the separation of charge being particularly large in (I*a*), whereas a 6-substituted pteridine can form the polarized structure (II) only, if a negative charge is located on a nuclear nitrogen atom and a positive charge on the substituent. 2- and 4-Substituted pteridines can form the polarized transannular structures (III) and (IV*a*) respectively, but in neither case is the separation of charge as large as in (I*a*). If the polarized structures (I—IV) make an important contribution to the excited states of the monosubstituted pteridines in the 300-mμ transition, then the intensity of that transition may be expected to be the highest in the 7-substituted pteridines and lowest in the 6-substituted, as the separation of charge during the transition is the greatest in the former and the smallest in the latter. Further, such a large separation of charge in the 7-substituted pteridines during the 300-mμ transition would require a larger amount of energy than is necessary for the other monosubstituted pteridines, thus accounting for the fact that a given 7-substituent in pteridine exerts a smaller bathochromic effect on the 300-mμ band than when it is placed elsewhere β to the bridge carbon atoms, namely, in the 2- or the 6-position.


(I*a*)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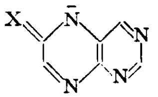
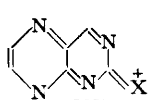

(II)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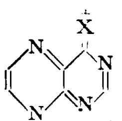
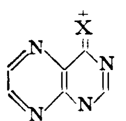

(IV*a*)


(IV*b*)

A substituent exerts its greatest bathochromic effect on the low-intensity 235-mμ band of the pteridine spectrum when in the 4-position, and the band becomes well defined in this case, showing fine structure (Fig. 2), whilst it remains a shoulder on the side of the higher-intensity band at shorter wavelengths, or is submerged under that band, when the substituent is elsewhere. The 4-substituted pteridines may form excited structures (IV*a* and IV*b*) with a more extended conjugation along the short axis of the molecule than is possible with other monosubstituted pteridines. Accordingly, it is likely that the 235-mμ transition in the pteridine spectrum is polarized along the short axis of the molecule whilst the 300-mμ transition is polarized along the long axis.

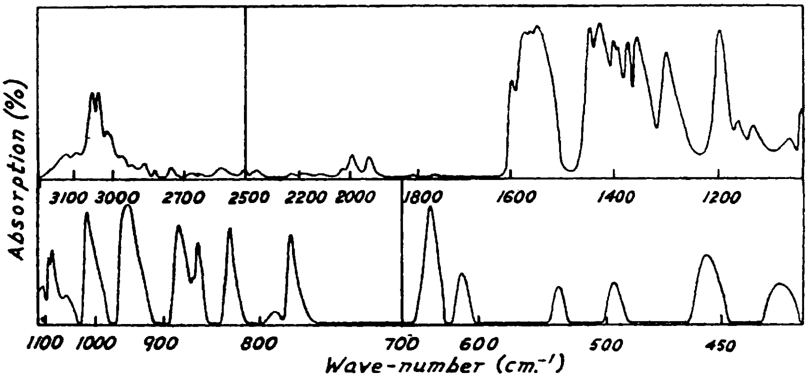
Pteridine and its monosubstituted derivatives exhibit, in *cyclo*hexane solution, fine structure in the long-wave band of the π-electron spectrum, and in some cases the $n \longrightarrow \pi$ and the second and third $\pi \longrightarrow \pi$ bands as well. The character of the fine structure in the long-wave band varies with the nature of the substituent rather than its position, whilst fine structure in the other bands depends on the position of the substituent, for it is confined almost exclusively to the spectra of the 4-substituted pteridines. The methoxypteridines, for example, show an alternation in the intensity and spacing of the fine-structure peaks of the long-wave band in their π-electron spectra (Fig. 2, Table 1), suggesting that principally two vibrations are active in the transition. Some alternation in the intensities of the fine-structure peaks of this band is observed in the spectra of the chloropteridines; and in those of the methylthio- and the dimethylamino-pteridines, where the fine structure is not sharp, the spacings between the peaks are twice as large as those found in the first $\pi \longrightarrow \pi$ band of the other monosubstituted pteridines, spacings which may arise from the submergence of alternant low-intensity peaks. The fine-structure spacings in this band lie in the range of 400—850 cm.$^{-1}$ for pteridine and its methyl-, chloro-, and methoxy-derivatives, a range which covers mainly nuclear bending and distortion vibrations. Spacings of the same order are observed in the third $\pi \longrightarrow \pi$ band of 4-methylthio- and 4-dimethylamino-pteridine (760 and 610 cm.$^{-1}$ respectively), whilst spacings twice as large are found in the second $\pi \longrightarrow \pi$ band of the 4-substituted pteridines, where again the fine structure is not sharp and the apparently large spacings may be due to the submergence of low-intensity peaks. Fine structure in the $n \longrightarrow \pi$ band, which occurs in the spectra of pteridine and its 4-methyl- and 4-methoxy-derivatives, is not so well defined as that of the first $\pi \longrightarrow \pi$ band, but the intensities of the individual peaks in the $n \longrightarrow \pi$ band are more regular and the spacings more uniform (500—550 cm.$^{-1}$), suggesting that a single vibration may be active in the transition, as would be expected in view of the localized character of the non-bonding electron orbital (Kasha, *loc. cit.*).

TABLE 2. *Infrared absorption bands (cm.$^{-1}$) of pteridine between* 4000 *and* 400 *cm.$^{-1}$.*

s = strong, m = medium, w = weak absorption.

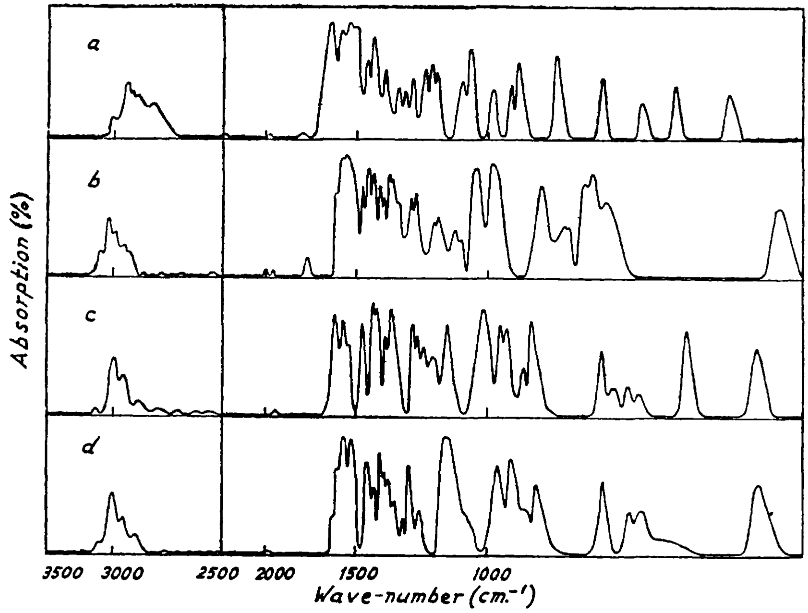
3117 w, 3090 w, 3055 m, 3035 m, 3013 w, 2951 w, 2917 w, 2854 w, 2806 w, 2784 w, 2670 w,
2636 w, 2568 w, 2508 w, 2445 w, 2240 w, 2170 w, 2115 w, 2025 w, 2000 w, 1940 w, 1820 w,
1763 w, 1603 m, 1580 s, 1573 s, 1558 s, 1461 s, 1435 s, 1400 s, 1391 s, 1368 s, 1348 s,
1286 s, 1197 s, 1176 w, 1158 w, 1109 w, 1092 m, 1085 m, 1056 w, 1015 s, 933 s, 882 s,
860 s, 822 s, 795 w, 777 s, 653 s, 616 m, 533 m, 497 m, 455 m, 434 m

FIG. 3. *Infrared spectrum of pteridine.*



Infrared Spectra.—Pteridine possesses thirty-six possible modes of vibration, and, the molecule being of low symmetry, most of these vibrations should be active in the infrared. The infrared absorption spectrum of pteridine exhibits some fifty bands between 3500 and 400 cm.$^{-1}$ (Fig. 3, Table 2), the twenty or so weak bands above 1600 cm.$^{-1}$ probably including many overtone or combination absorptions. Between 400 and 700 cm.$^{-1}$ pteridine gives rise to six absorption bands, which, by analogy with the assigned bands in the same region of the naphthalene spectrum (Lippincott and O'Reilly, *J. Chem. Phys.*, 1955, **23**, 238), are likely to be due to skeletal vibrations. Of the seven bands in the pteridine spectrum between 700 and 1050 cm.$^{-1}$, that at 777 cm.$^{-1}$ is connected with the presence of a 4-C–H bond, and may be due to the out-of-plane bending vibration of that bond, since a corresponding band is found in the spectra of all of the 2-, 6-, and 7-monosubstituted pteridines examined, but not in the spectra of any 4-monosubstituted pteridine (Fig. 4, Table 3). Similarly the 860- and 882-cm.$^{-1}$ bands in the spectrum of pteridine may arise from the 6- and 7-C–H bending vibrations, as corresponding bands are observed in the spectra of the 2- and 4-monosubstituted pteridines, but not in the spectra of the 6- or 7-substituted derivatives, except for 6- and 7-dimethylaminopteridine, which absorb at 880 and 888 cm.$^{-1}$ respectively. 6- and 7-Aminopteridine * do not absorb in this region, so the 880- and 888-cm.$^{-1}$ bands in the dimethylamino-derivatives are probably due to a vibration of the substituent group. However, the 860-cm.$^{-1}$ band is absent from the spectra of most of the 2-substituted pteridines also, indicating that the 2-H–C bond is probably involved in the vibration giving rise to this band. It is unusual that the two adjacent C–H bonds in the 6- and the 7-position of pteridine should undergo out-of-plane deformation vibrations which absorb at a higher frequency than the corresponding vibration of the single C–H bond in the 4-position, since the normal ranges of 860—900 cm.$^{-1}$ for one free hydrogen atom, and 800—860 cm.$^{-1}$ for two adjacent hydrogen atoms attached to an aromatic nucleus, seem to obtain even in heterocyclic systems (Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen, London, 1954, p. 235). Indeed the value of 777 cm.$^{-1}$ for the proposed 4-C–H distortion vibration is low even for a single hydrogen atom attached to an ethylenic system, a group which absorbs in the range 790—840 cm.$^{-1}$ (Bellamy, *op. cit.*, p. 31). There is some doubt whether the 777-, 860-, and 882-cm.$^{-1}$ bands of the pteridine spectrum are due to C–H deformation vibrations since comparable bands at 784, 868, and 874 cm.$^{-1}$ occur in the spectrum of tetrachloropteridine, though it is possible that the latter set is due to C–Cl stretching vibrations.

FIG. 4. *Infrared spectrum of* (*a*) *2-dimethylamino-,* (*b*) *4-chloro-,* (*c*) *6-methoxy-, and* (*d*) *7-methylthio-pteridine.*



In the same region, pteridine also shows bands at 822, 933, and 1015 cm.$^{-1}$, probably due to skeletal vibrations as corresponding bands are found in the spectra of all of the substituted pteridines examined. The 822-cm.$^{-1}$ band is particularly well marked in intensity and position, and displays an interesting substitution effect. The corresponding band in the pteridines substituted β to the bridge carbon atoms lies in the range 817—

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* It is hoped to discuss the ultraviolet and infrared absorption spectra of the pteridines substituted with a potentially tautomeric group in a later paper.

TABLE 3. *Infrared absorption bands (cm.*$^{-1}$*) of some substituted pteridines between 2000 and 700 cm.*$^{-1}$*.*

2-Methyl	4-Methyl	7-Methyl	2-Chloro	4-Chloro	2-Methoxy	4-Methoxy	6-Methoxy	7-Methoxy
2000 (w)	2000 (w)	1990 (w)	2000 (w)	2000 (w)	2050 (w)	1985 (w)	1905 (w)	1955 (w)
1915 (w)	1940 (w)	1945 (w)	1570 (s)	1940 (w)	1598 (s)	1578 (s)	1591 (s)	1930 (w)
1590 (s)	1567 (s)	1585 (m)	1564 (s)	1710 (w)	1560 (s)	1570 (s)	1560 (s)	1860 (w)
1570 (s)	1558 (s)	1567 (s)	1544 (s)	1570 (m)	1543 (s)	1555 (s)	1546 (m)	—
1552 (s)	1546 (s)	1556 (s)	1445 (m)	1558 (s)	1494 (s)	1497 (s)	1472 (s)	1591 (m)
1442 (s)	1473 (m)	1526 (w)	1430 (s)	1540 (s)	1450 (s)	1471 (m)	1394 (s)	1570 (s)
1389 (m)	1458 (s)	1436 (s)	1424 (s)	1458 (m)	1393 (s)	1444 (w)	1374 (s)	1560 (s)
1375 (m)	1436 (m)	1407 (w)	1363 (m)	1423 (s)	1347 (w)	1420 (m)	1333 (m)	1546 (s)
1338 (m)	1399 (w)	1389 (m)	1345 (m)	1393 (s)	1326 (w)	1406 (s)	1298 (s)	1487 (m)
1312 (m)	1374 (m)	1361 (s)	1328 (m)	1359 (m)	1276 (m)	1372 (m)	1212 (s)	1468 (s)
1254 (s)	1357 (w)	1342 (m)	1304 (w)	1336 (w)	1240 (w)	1349 (s)	1195 (m)	1394 (s)
1192 (w)	1330 (w)	1295 (w)	1289 (m)	1310 (s)	1203 (m)	1305 (w)	1172 (m)	1372 (s)
1153 (m)	1304 (w)	1270 (s)	1261 (w)	1295 (s)	1186 (w)	1279 (w)	1141 (m)	1321 (m)
1102 (w)	1260 (s)	1221 (w)	1244 (w)	1218 (m)	1168 (m)	1222(w)	1100 (s)	1307 (s)
1079 (w)	1215 (w)	1201 (s)	1210 (s)	1200 (m)	1131 (w)	1184 (w)	1010 (s)	1281 (m)
1038 (s)	1117 (w)	1162 (s)	1172 (w)	1136 (w)	1080 (w)	1172 (m)	975 (s)	1207 (s)
1024 (m)	1080 (s)	1098 (m)	1160 (w)	1126 (w)	1043 (s)	1118 (s)	964 (s)	1191 (m)
1006 (m)	1029 (w)	1089 (m)	1129 (s)	1077 (w)	1018 (s)	1024 (s)	932 (w)	1115 (w)
966 (m)	1015 (s)	1036 (m)	1091 (w)	1062 (w)	983 (w)	986 (w)	920 (s)	1104 (w)
951 (s)	997 (w)	1006 (w)	1016 (s)	1026 (s)	963 (w)	970 (s)	824 (m)	1018 (s)
910 (w)	972 (w)	956 (s)	988 (w)	991 (s)	948 (s)	891 (s)	811 (w)	971 (m)
885 (s)	958 (m)	915 (s)	971 (w)	903 (s)	889 (m)	882 (m)	795 (w)	963 (m)
829 (s)	888 (s)	829 (s)	951 (s)	870 (w)	880 (w)	860 (m)	784 (w)	935 (s)
788 (s)	860 (s)	800 (m)	890 (s)	862 (w)	866 (m)	855 (s)	741 (s)	823 (m)
759 (w)	835 (s)	790 (m)	828 (m)	844 (s)	829 (s)	839 (s)	688 (s)	810 (w)
741 (s)	705 (w)	702 (w)	785 (s)	835 (s)	793 (m)	742 (s)	—	790 (m)
689 (s)	—	678 (s)	716 (m)	820 (m)	758 (s)	715 (s)	—	720 (s)
—	—	—	—	678 (m)	746 (w)	—	—	—

2-Methyl-thio	4-Methyl-thio	7-Methyl-thio	2-Dimethyl-amino	4-Dimethyl-amino	6-Dimethyl-amino	7-Dimethyl-amino	2 : 4 : 6 : 7-Tetra-chloro
1580 (s)	1980 (w)	1985 (w)	1970 (w)	1945 (w)	1930 (w)	1985 (w)	2000 (w)
1561 (s)	1945 (w)	1586 (w)	1740 (w)	1580 (s)	1596 (s)	1915 (w)	1697 (m)
1537 (s)	1570 (m)	1573 (m)	1610 (s)	1558 (s)	1560 (s)	1601 (m)	1567 (s)
1434 (s)	1555 (s)	1555 (s)	1570 (s)	1540 (s)	1537 (s)	1560 (s)	1546 (s)
1367 (m)	1537 (s)	1525 (s)	1540 (s)	1522 (s)	1506 (m)	1525 (s)	1516 (s)
1349 (w)	1457 (s)	1434 (s)	1528 (s)	1493 (s)	1435 (m)	1435 (s)	1397 (s)
1290 (m)	1428 (s)	1387 (m)	1444 (m)	1420 (m)	1393 (s)	1417 (s)	1379 (s)
1281 (m)	1391 (s)	1353 (s)	1425 (s)	1408 (s)	1340 (w)	1398 (s)	1281 (s)
1222 (m)	1321 (m)	1330 (s)	1337 (m)	1387 (m)	1300 (w)	1382 (s)	1270 (s)
1216 (s)	1304 (s)	1312 (m)	1275 (w)	1330 (m)	1256 (m)	1370 (s)	1237 (s)
1161 (w)	1283 (s)	1305 (m)	1246 (m)	1313 (s)	1221 (w)	1339 (s)	1200 (s)
1139 (w)	1220 (m)	1283 (w)	1217 (m)	1275 (s)	1164 (m)	1280 (w)	1190 (m)
1129 (s)	1194 (w)	1236 (w)	1167 (m)	1254 (m)	1103 (m)	1250 (m)	1141 (s)
1024 (s)	1158 (w)	1227 (s)	1150 (m)	1208 (m)	1062 (w)	1230 (w)	1073 (w)
1017 (s)	1127 (w)	1184 (w)	1132 (m)	1150 (w)	1012 (s)	1172 (m)	1035 (s)
976 (m)	1053 (w)	1097 (s)	1057 (m)	1098 (s)	940 (s)	1123 (w)	980 (w)
958 (w)	1030 (s)	1024 (w)	1042 (s)	1064 (w)	918 (w)	1100 (m)	874 (s)
943 (s)	997 (s)	978 (s)	990 (m)	1032 (m)	880 (m)	1065 (w)	868 (m)
900 (w)	980 (m)	953 (s)	955 (m)	984 (w)	817 (m)	1002 (m)	813 (m)
877 (m)	891 (m)	928 (w)	943 (s)	950 (w)	787 (m)	937 (s)	784 (m)
824 (s)	875 (w)	910 (m)	883 (s)	878 (m)	697 (m)	917 (w)	725 (m)
780 (s)	843 (s)	821 (m)	822 (m)	860 (s)	683 (s)	888 (s)	—
712 (m)	834 (s)	791 (m)	791 (m)	851 (m)	—	818 (s)	—
—	—	779 (m)	750 (m)	834 (s)	—	783 (m)	—
—	—	758 (w)	710 (m)	715 (m)	—	713 (w)	—
—	—	686 (s)	—	—	—	—	—

829 cm.$^{-1}$ and, in the pteridines substituted α to those atoms, between 834 and 839 cm.$^{-1}$. It seems, therefore, that the 822-cm.$^{-1}$ vibration of pteridine involves mainly the movement of the nuclear atoms of the molecule, the movement perhaps being that of the atoms α to the bridge carbon atoms of the pteridine rings, because substituents attached to such an α atom displace the band to a greater degree than the same substituents attached to a β atom. The 933- and 1015-cm.$^{-1}$ bands of the pteridine spectrum vary more widely in position than the 822-cm.$^{-1}$ band in the spectra of the substituted pteridines, probably owing to greater involvement of the extranuclear atoms in the vibrations giving rise to these bands.

Between 1050 and 1180 cm.$^{-1}$ in the spectrum of pteridine occur six bands of moderate or weak intensity, which are likely to be due to C–H bending vibrations, since comparable bands are not observed in the spectrum of tetrachloropteridine and such vibrations in other aromatic systems absorb in the same region. The spectra of the monosubstituted pteridines exhibit similar bands in the same region, but, unlike the case of the substituted benzenes, the locations of these bands do not seem to be characteristic of the particular positions of substitution.

From 1200 to 1500 cm.$^{-1}$ the spectra of pteridine and its derivatives are complex, and no satisfactory correlations between the spectra can be made. In the ring-stretching vibration region, three bands are observed in the spectra of all of the pteridine derivatives examined in the ranges 1610—1565, 1570—1545, and 1560—1515 cm.$^{-1}$ respectively. Substituents containing comparatively heavy atoms linked immediately to the nucleus, namely, the chloro- and methylthio-groups, displace the 1610—1565-cm.$^{-1}$ band towards the lower extremity of its range, just as they lower the frequency of the 1600-cm.$^{-1}$ ring-stretching vibration in benzene (Bellamy, *op. cit.*, p. 60). Moreover, the frequency of the 1610—1565-cm.$^{-1}$ band for a given substituent is highest when it is in the 2-position, though not much higher than when in the 6- or the 7-position, and lowest when in the 4-position. It seems likely, therefore, that the 1610—1565-cm.$^{-1}$ band in the spectra of the pteridines is due to a ring-stretching vibration which involves the movement of atoms immediately attached to the nucleus, particularly those substituted in the 4-position. The position of the 1610—1565-cm.$^{-1}$ band in the spectra of the monosubstituted pteridines is also affected by the mesomeric capacity of the substituent. For substituents in which the masses of the atoms directly attached to the nucleus are of the same order, the frequency of the band, for a given position of substitution, increases with the mesomeric effect of the substituent in the sequence: $\text{Me} < \text{OMe} < \text{NMe}_2$ and $\text{Cl} \ll \text{SMe}$. The mesomeric effect of these substituents enhances the π-electron density of the pteridine nucleus, and so strengthens the nuclear bonds, producing ring-stretching vibrations of higher frequencies.

Between 1650 and 2800 cm.$^{-1}$ the spectra of pteridine and its derivatives show a number of weak bands which are probably due to overtone and combination absorptions. The absorption pattern between 1650 and 2000 cm.$^{-1}$ in the substituted pteridines, unlike that in the benzene series, does not seem to be characteristic of the substitution type. Finally, in the C–H stretching vibration region, pteridine gives rise to two moderately intense bands of 3035 and 3055 cm.$^{-1}$ with weaker bands on either side, whilst the monosubstituted pteridines show one moderately intense band, usually near 3050 cm.$^{-1}$.

EXPERIMENTAL

Materials.—The sources of the mono-, di-, and tri-substituted pteridines were as given by Albert, Brown, and Cheeseman (*J.*, 1951, 474; 1952, 1620, 4219) and Albert, Brown, and Wood (*J.*, 1954, 3832). 2 : 4 : 6 : 7-Tetrachloropteridine was prepared by the method of Shöpf, Reichert, and Riefstahl (*Annalen*, 1941, **548**, 82).

Ultraviolet Spectra.—These were measured with a Hilger Uvispek H700/301 Quartz Spectrophotometer, using *cyclo*hexane solutions and buffer solutions with the pH values recorded in Table 1. The buffer solutions were 0·01M-glycine (for pH 1·5—3·5), 0·01M-acetate (for pH 3·8—5·7), 0·01M-phosphate (for pH 6·0—7·9), together with N- (pH 0) and 0·1N-hydrochloric acid (pH 1·0).

Infrared Spectra.—These were measured with a Perkin-Elmer model 12C spectrometer, with prisms of lithium fluoride, sodium chloride, and potassium bromide. The compounds were examined as solids included in pressed potassium bromide discs.

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