LXXVIII.—*Ultra-violet Absorption Spectra of Some Closed Chain Carbon Compounds. Part II. Dimethylpyrazine, Hexamethylene, and Tetrahydrobenzene.*

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In a former paper (Trans., 1898, 73, 598), we gave the results of the examination of the absorption spectra of thiophen, pyrrole, furfuran, and some of the more important furfuran derivatives. Each of these compounds contains two pairs of carbon atoms doubly linked, the chain being closed by a polyvalent element other than carbon. No trace of selective absorption, such as is shown by benzene, pyridine, and many of their derivatives, could be detected in the spectra of any of these substances.

We have now extended our investigation to 2:5-dimethylpyrazine,

a substance in which not merely one carbon is replaced by nitrogen in the benzene ring, as in pyridine, but two. It thus belongs to a group not previously examined.

From the analogy between the constitution of this substance and that of pyridine, it was anticipated that it would show a marked selective absorption, and this anticipation proved to be correct. One of the principal reasons for examining a substance of this constitution lay in the fact that whilst pyridine contains the group $\cdot\text{C}:\text{N}\cdot$ once in the benzene structure, dimethylpyrazine contains it twice, and the original formula proposed for cyanuric acid (Trans., 1882, 41, 84) contains it three times; accordingly, if this formula were correct for cyanuric acid and its esters, we should expect that they would exhibit a powerful absorption band, more intense than that of pyrazine, just as that of pyrazine is more intense than that of pyridine. But it has been concluded, from a widely extended experience of the behaviour of such substances under the ultra-violet rays, and particularly from the results of a recent examination of the absorption spectra of its derivatives (Hartley, *Proc.*, 1899, 15, 46), that cyanuric acid does not possess this structure, but one in which

the acid is represented by a ring composed of three $\begin{array}{c} \cdot\text{N}\cdot\text{C}\cdot\text{O} \\ | \\ \text{H} \end{array}$ groups, a mode of single linking resembling that of a hydropyridine or of a hydroaromatic group with one carbon replaced by nitrogen (*Phil.*

Trans., Part II, 1885, 519); it should not therefore exhibit selective absorption.

The specimen of dimethylpyrazine used in the experiments was prepared by the reduction of isonitrosoacetone in accordance with the directions given by Gabriel and Pinkus (*Ber.*, 1893, 26, 2206). It boiled constantly at 154–155° (corr.) under atmospheric pressure.

2:5-Dimethylpyrazine.

Curves of Molecular Vibrations.

A layer, 25 mm. thick, of a solution of dimethylpyrazine containing 1 mill.-mol. in 100 c.c. of absolute alcohol cuts off all rays beyond $1/\lambda$ 2994. On reducing the thickness of the layer to 10 mm., an absorption band makes its appearance, reaching from $1/\lambda$ 3064 to $1/\lambda$ 4321. This band is very persistent, and is still traceable in a layer 1 mm. thick of a solution containing 1 mill.-mol. of the

substance dissolved in 500 c.c. alcohol. The band of dimethylpyrazine is thus both wider and also more persistent than that of pyridine. These results are shown in the curve on page 847.

In the paper already referred to, an account was also given of the absorption spectra of diketohexamethylene. Previous investigations had shown that piperidine (Hartley, Trans., 1885, 47, 691) and hexachlorobenzene (Hartley, Trans., 1881, 39, 153) exhibit continuous absorption, but show no absorption band, and, as was to be expected, diketohexamethylene, in which the six carbon atoms are united with each other by a single bond, as in hexachlorobenzene and piperidine, likewise showed no bands in the spectrum.

Through the kindness of Prof. Sydney Young and Miss Fortey, we have recently been enabled to examine a specimen of pure hexamethylene prepared from Galician petroleum. This substance, in comparison with benzene and pyridine, is highly diactinic. A layer, 60 mm. thick, of a solution containing 1 mill.-mol. dissolved in 20 c.c. of alcohol, transmits all rays up to $1/\lambda$ 3920, whilst a layer of the same solution, 10 mm. thick, transmits practically the whole spectrum. In none of the photographs of the spectra of this substance could any trace of a banded structure be detected.

Professor Young and Miss Fortey were also good enough to place a specimen of pure tetrahydrobenzene in our hands for examination. This substance exhibits somewhat greater general absorption than hexamethylene, a layer, 60 mm. thick, of a solution containing 1 mill.-mol. in 20 c.c. alcohol absorbing all rays beyond $1/\lambda$ 3694, while absorption is still traceable in a layer of the same solution 1 mm. thick. Like hexamethylene, tetrahydrobenzene shows no selective absorption. The examination of these two substances thus confirms the conclusion previously reached, that the banded spectrum is shown only by substances which possess the true benzenoid structure (Hartley, Trans., 1881, 39, 153).

Dimethylpyrazine, C₆H₈N₂.

0.108 gram (1 milligram-mol.) in 100 c.c. alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$1/\lambda$.	λ .
25	Spectrum continuous to Complete absorption beyond.	2994	3340
20	Spectrum continuous to Complete absorption beyond.	2994	3340
15	The same.		

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0.108 gram (1 milligram-mol.) in 100 c.c alcohol (*continued*).

Thickness of layer of liquid in millimetres.	Description of spectrum.	$1/\lambda$.	λ .
10	Spectrum continuous to	3064	3263
	Absorption band	3064 to 4321	3263 to 2314
	Strong rays transmitted from 4321 to ..	4443	2314 to 2250
5	Spectrum continuous to	3076	3250
	Absorption band	3076 to 4242	3250 to 2357
	Strong rays transmitted partially from 4242 to	4539	2357 to 2203
	Complete absorption beyond.		
4	Spectrum continuous to	3076	3250
	The same as 5, excepting a faint transmission of rays at	4112 and 4128	2431 and 2422
3	Spectrum continuous to	3148	3176
	Absorption band	3148 to 4112	3176 to 2431
	Spectrum transmitted from 4112 to ...	4555	2431 to 2195
	Complete absorption beyond.		
2	Spectrum continuous to	3188	3136
	Absorption band	3188 to 4089	3136 to 2445
	Spectrum continuous, but weak from 4089 to.....	4555	2445 to 2195
	Complete absorption beyond.		
1	Spectrum continuous to	3319	3012
	Absorption band	3319 to 3999	3012 to 2500
	Weak spectrum from 3999 to	4555	2500 to 2195
	Complete absorption beyond.		

Dimethylpyrazine (*continued*).

0.108 gram (1 milligram-mol.) in 500 c.c. alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$1/\lambda$.	λ .
4	Spectrum continuous to ...	3349	2985
	Absorption band ..	3349 to 3877	2985 to 2579
	Rays faintly visible between	3382 and 3483	2956 and 2871
	Spectrum ends at	3999	4555
3	Spectrum continuous to	3520	2840
	Absorption band	3520 to 3818	2840 to 2619
	Faint transmission of a strong line at ..	3818	2619
	Continuous spectrum from 3877 to.....	4555	2579 to 2195
2	Spectrum continuous to	3520	2840
	Absorption band	3520 to 3816	2840 to 2620
	Continuous spectrum 3816 to	4555	2620 to 2195
1	Spectrum continuous to	3563	2806
	Strong lines feebly transmitted to	3748	2668
	Absorption band	3563 to 3816	2806 to 2620
	Continuous spectrum 3816 to	4555	2620 to 2195
	Transmission of a continuous spectrum on further dilution of solution.		

Hexamethylene, C₆H₆·H₆.

0.084 gram (1 milligram-mol.) in 20 c.c. alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$1/\lambda$.	λ .
60	Spectrum continuous to..... Complete absorption beyond, except for the feeble transmission of strong lines at.....	3920 4112 4125	2551 2431 2424
45	Spectrum continuous to..... Faint prolongation to.....	4125 4413	2424 2266
30	The same as 45.		
25	The same as 30, but stronger; lines transmitted faintly at	4540 4555	2202 2195
20	Spectrum continuous to..... But faint beyond.....	4555 4413	2195 2266
15	The same as 20.		
10	Spectrum continuous to	4555	2195
5	A strong line feebly transmitted at	4656	2147
4	The same as 10. Spectrum continuous.		

Tetrahydrobenzene, C₆H₆·H₄.

0.082 gram (1 milligram-mol.) in 20 c.c. alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$1/\lambda$.	λ .
60	Spectrum continuous to.....	3694	2707
45	Same as 60.		
30	Spectrum continuous to.....	3886	2573
25	" "	3892	2569
20	" "	3921	2550
15	" "	4029	2482
10	" "	4125	2424
5	Same as 10; very feeble prolongation to.....	4321	2314
4	Same as 5; " "	4413	2266
3	Same as 4, but somewhat stronger.		
2	Spectrum continuous to..... Strong lines transmitted at	4413 4536	2266 2205
1	The same, but somewhat stronger.	4555	2195

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