THE RAMAN SPECTRA OF DIOXANE AND TETRALIN.

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1. Introduction.

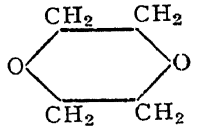
In spite of the fact that organic compounds generally give rather complicated Raman spectra, the extensive researches in this field carried out in the last few years have enabled, in many cases, the modified lines to be classified into groups which can be identified as due to certain characteristic groups or chemical bonds in the molecule. In order to interpret the results in relation to the molecular structure, it is important to obtain the Raman spectra of the compounds studied as completely as possible. The simple ring compounds repeatedly investigated by several workers include benzene, cyclohexane and naphthalene. But comparatively little work has been done in other cyclic compounds possessing a somewhat similar structure. The present paper gives the results obtained by the author with dioxane and tetralin.

Explanation of Symbols.

Symbol	Wavelength	Wavenumber
a	3650	27358
b	3655	27353
d	4047	24705
e	4078	24516
f	4339	23039
g	4348	22995
h	4358	22938

TABLE I.

The Raman frequencies of Dioxane from 4047 Å. U.—5100 Å. U.



No.	Raman lines		$\Delta\nu$ in cm.$^{-1}$	Intensity		Assignment
	λ	ν		Without filter	With filter	
1	4062·5	24609	2779	1	..	*a*
2	4067·3	24580	2773	0	..	*b*
3	4076·6	24523	2863	4	..	*a*
4	4086·8	24462	243	2	..	*d*
5	4092·7	24427	2961	6*b*	..	*a*
6	4099·5 (double)	24387	$\overline{1449}$	3*b*	1	*h*
7	4111·7	24314	3075	1	..	*a*
8	4116·6	24285	421	0	..	*d*
9	4118·5	24273	433	3	..	*d*
10	4127·6	24220	485	5	..	*d*
11	4140·1	24147	$\overline{1209}$	0	..	*h*
12	4148·7	24097	419	0	..	*e*
13	4156·8	24050	466	0*b*	..	*e*
14	4188·5	23868	837	8*sh*	2	*d*
15	4191·1	23854	851	1*sh*	..	*d*
16	4204·7	23771	$\overline{835}$	3	1	*h*
17	4207·7	23759	946	0	..	*d*
18	4220·2	23689	1016	8	0	*d*
19	4221·4	23682	834	2	..	*e*
20	4237·1	23596	1109	3	..	*d*

TABLE I (*contd.*)

No.	Raman lines		$\Delta\nu$ in cm.$^{-1}$	Intensity		Assignment
	λ	ν		Without filter	With filter	
21	4240·3	23576	1129	3	..	*d*
22	4255·0	23495	1210	0	..	*d*
23	4256·8	23485	1221	5	0	*d*
24	4272·5	23399	1306	6	0	*d*
25	4277·4	23372	1333	2	..	*d*
26	4291·1	23297	1219	1	..	*e*
27	4297·8	23261	1444	6	0	*d*
28	4306·0	23249	1455	0	..	*d*
29	4307·9	23207	1299	0	..	*e*
30	4393·0	22757	181?	0	..	*h*
31	4441·0	22512	426	0	0	*h*
32	4442·3	22504	434	2	2	*h*
33	4451·6	22458	480	4	3	*h*
34	4523·2	22102	836	10*sh*	8	*h*
35	4525·6	22090	848	0	0	*h*
36	4535·2	22044	2662	1	..	*d*
37	4546·7	21988	2718 950	3 0	0	*d* *h*
38	4554·5	21950	2756	0	..	*d*
39	4560·3	21922	2783 1006	6	4	*d* *h*
40	4576·3	21846	2860 1109	8	2	*d* *h*
41	4582·2	21818	2888 1120	3	1	*d* *h*

TABLE I (*concld.*)

No.	Raman lines		$\Delta\nu$ in cm.$^{-1}$	Intensity		Assignment
	λ	ν		Without filter	With filter	
42	4597·7	21744	2962	10	1	*d*
43	4600·8	21729	1209	1	..	*h*
44	4603·4	21717	1221	6	4	*h*
45	4616·8	21654	2863	3	..	*e*
46	4621·4	21632	3074 1306	8	4	*d* *h*
47	4626·2	21610	1328	2	1	*h*
48	4640·3	21544	2973	3(*b*)	..	*e*
49	4650·8	21496	1442	8	6	*h*
50	4652·6	21487	1451	0	0	*h*
51	4929·6	20279	2659	1	1	*h*
52	4944·5	20220	2718	1	1	*h*
53	4960·7	20153	2785	3	2	*h*
54	4980·9	20071	2867	8	6	*h*
55	4986·1	20050	2888	2	1	*h*
56	4991·6	20027	2968	1	0	*g*
57	5006·0	19970	2968	8*b*	8	*h*
58	5032·8	19864	3074	1	0	*h*

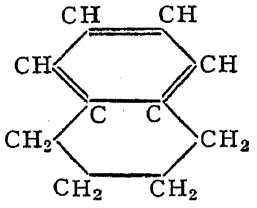
2. *Experimental Arrangements and Results.*

The experimental set up was the same as that previously used in the investigations of the author.[1] The two liquids used in this investigation were those used for the measurements of dipole moments at the Institute

[1] Venkateswaran, C. S., *Proc. Ind. Acad. Sci.*, 1935, **1**, 850.

TABLE II.

The Raman frequencies of Tetralin from 4047 Å. U.—5100 Å. U.



No.	Raman lines		$\Delta\nu$ in cm.$^{-1}$	Intensity		Assignment
	λ	ν		Without filter	With filter	
1	4071·7	24553	153	6	1	*d*
2	4089·1	24448	258	2	0	*d*
3	4095·5	24410	2944	1	..	*b*
4	4104·6	24356	$\overline{1418}$	0	..	*h*
5	4117·6	24279	427	2	0	*d*
6	4119·9	24266	440	2	..	*d*
7	4123·2	24246	460	0	..	*d*
8	4130·8	24202	504	1	..	*d*
9	4139·9	24148	557	0	..	*d*
10	4143·8	24128	578	3	..	*d*
11	4164·6	24005	701	1	..	*d*
12	4168·1	23985	721	8	2	*d*
13	4176·5	23946	760	0	..	*d*
14	4181·8	23906	800	1	..	*d*
15	4184·5	23891	815	2	..	*d*
16	4200·8	23798	908	2	..	*d*
17	4214·0	23724	982	0	..	*d*
18	4223·2	23672	1034	10	3	*d*
19	4228·0	23645	1061*	0	..	*d*

* An asterisk mark against some of the frequency numbers shows that they possess a doublet structure.

TABLE II (*contd.*)

No.	Raman lines		$\Delta\nu$ in cm.$^{-1}$	Intensity		Assignment
	λ	ν		Without filter	With filter	
20	4239·0	23584	1122	0	..	*d*
21	4245·8	23546	1160	1	..	*d*
22	4253·1	23506	1200	8	2	*d*
23	4258·4	23476	1230*	0	..	*d*
24	4268·2	23421	1285	3	..	*d*
25	4277·0	23369	1336	3	..	*d*
26	4279·5	23360	$\overline{422}$	0	2	*h*
27	4285·7	23327	1379	2	..	*d*
28	4293·8	23278	1427	6	1	*d*
29	4298·4	23258	1448	1	..	*d*
30	4307·9	23207	1499	0	..	*d*
31	4309·7	23197	$\overline{259}$	1	2	*h*
32	4322·0	23130	1575	0	..	*d*
33	4326·6	23106	1600	8	2	*d*
34	4329·3	23092	$\overline{154}$	4	4	*h*
35	4387·9	22784	154	5	8	*h*
36	4408·1	22680	258	3	4	*h*
37	4409·9	22670	268	..	0	*h*
38	4440·0	22511	427	3	6	*h*
39	4443·1	22500	438	..	0	*h*
40	4446·0	22486	457	1	4	*h*

* An asterisk mark against some of the frequency numbers shows that they possess a doublet structure.

TABLE II (*contd.*)

No.	Raman lines		$\Delta\nu$ in cm.$^{-1}$	Intensity		Assignment
	λ	ν		Without filter	With filter	
41	4455·4	22438	505	2	5	*h*
42	4467·0	22380	558	0	1	*h*
43	4470·5	22363	575	3	4	*h*
44	4495·0	22241	697	1	1	*h*
45	4499·6	22218	720	8	10	*h*
46	4508·1	22176	762	0	0	*h*
47	4515·8	22138	800	0	1	*h*
48	4518·7	22124	814	1	2	*h*
49	4537·0	22035	903	..	0	*h*
50	4544·1	22004	1035	0	0	*f*
51	4552·7	21959	1035 979	0	2	*g, h*
52	4560·3	21903	1035	8	10	*h*
53	4570·3	21874	1064*	3	2	*h*
54	4576·9	21843	2863	1	..	*d*
55	4584·5	21806	2902	1	..	*d*
56	4590·5	21778	2930 1160	4*b*	4	*d*
57	4594·0	21762	2943	0	0	*d*
58	4601·4	21726	1202	5	6	*h*
59	4607·0	21704	1234	0	1	*h*
60	4617·1	21653	3052 1285	6	3	*d, h*
61	4627·8	21602	1336	1	2	*h*

TABLE II (*concld.*)

No.	Raman lines		$\Delta\nu$ in cm.$^{-1}$	Intensity		Assignment
	λ	ν		Without filter	With filter	
62	4636·3	21563	1383	1	2	*h*
63	4647·4	21511	1427	6	6	*h*
64	4652·2	21489	1449	1	2	*h*
65	4662·8	21440	1498	0	0	*h*
66	4680·8	21362	1576	2	2	*h*
67	4685·1	21339	1599	3	4	*h*
68	4980·8	20071	2867	3	3	*h*
69	4989·8	20035	2903	1	1	*h*
70	4993·7	20020	2918	0	0	*h*
71	4998·3	20001	2937	6	6	*h*
72	5018·7	19920	3008	1	1	*h*
73	5025	19892	3046	10	10	*h*

and the author's thanks are due to Dr. M. A. Govinda Rau for kindly permitting the use of the extra-pure substances which he had carefully prepared for his work. In order to facilitate the proper assignment of the excited lines, spectrograms were taken with and without filters. An alcoholic solution of *p*-nitro-toluene was found to be an efficient filter which cut off almost completely the 4046 radiations while transmitting the 4358 radiations of the source with maximum intensity. For dioxane, an alkaline solution of *o*-cresolpthalin helped to clear up the 4916 region considerably. The filter was contained in an outer jacket surrounding the experimental tube as in Fig. 1. It would be of interest to mention that tubes with almost perfectly flat ends could be easily made in pyrex glass with the outer tube fused to the bottom and supported with a few spokes dug into its walls at the top. In order to prevent the evaporation of the filter solution when the tube was placed close to the arc, the top end was closed with plaster of Paris through which two small tubes were passed for the introduction of the solution. The

TABLE III.

The intensities given in the brackets are for the 4358 *excitations.*

Dioxane		Tetralin			Cyclohexane	Benzene
Author	Villars	Author	Mukerji	Bonino and Cella	Krishnamurti	Grassman and Weiler (Incomplete)
181(0)?	..	154(8)	162(3)	158(4)	..	..
243(1)	..	259(4)	265(2)	265(3)	381($\frac{1}{2}$)	
	291(0)	268(0)	..	..	..	
425(0)	..	427(6)	430(4)	432(2)	425(1)	404(1)
		439(0)	..	..		
433(2)	434(00)	459(4)	..	..		
482(4)	519(00)	505(5)	511(3)	513(3)		
		558(1)	561(2)	567(2)		
		577(4)	582(3)	585(3)		607(8)
		699(1)	699(2)	..	695(0)	692(1)
		720(10)	723(5)	724(4)		
		761(0)	752(1)	759(1)		781(0)
837(8)	837(4)	800(1)	..	..	804(10)	802(0)
849(1)	..	814(2)	814(2)	815(2)		824($\frac{1}{2}$)
			839(0)	848(0)		849(4)
		905(0)				
946(0)	..	980(1)	..	..		984(2)
						992(15)
1012(6)	..	1035(10)	1037(7)	1038(5)	1028(8)	1034(1)
		1063(3)	..	..		
1109(3)	..	1122(0)	..	..		
	1117(1)					
1124(3)		1163(4)	1174(0)	1160(1)	1156(1)	1176(4)
1209(1)	..	1201(6)	1205(6)	1204(4)		
1221(5)	1214(1)	1232(1)	..	..	1266(5)	
		1285(3)	1283(1)	1283(2)		1285(0)
1306(8)	..	..	..	..	..	..
1328(2)	..	1336(2)	..	1340(1$\frac{1}{2}$)	1344($\frac{1}{2}$)	1326($\frac{1}{2}$)
1444(8)	1442(2)	1427(6)	1433(3)	1433(3)	1444(5)	1403(2)

TABLE III (*contd.*)

Dioxane		Tetralin			Cyclohexane	Benzene
Author	Villars	Author	Mukerji	Bonino and Cella	Krishnamurti	Grassman and Weiler (Incomplete)
1451(1)	..	1448(2)	1458(5)	1456(3)		1449($\frac{1}{2}$)
		1499(0)	..	..		1480(0)
		1575(2)	1582(3)	1583(3)		1585(12)
		1600(4)	1602(3)	1602(3)		1606(8)
2660(1)	..	..	..	..	2662(1)	2615(2)
2718(1)	2720(00)	..	..	..		
2784(3)	..	..	..	..		
2863(8)	2864(3)	2865(4)	2865(4)	2862(2$\frac{1}{2}$)	2852(8)	..
2888(2)	..	2902(1)	..	..	2889(1)	..
2968(10)*b*	2967(3)	2937(6)	2940(4)	..	2922(8)	2949(4)
		3008(1)	..	..		3049(8)
3064(1)	..	3049(10)	3046(5)	3049(5)		3064(12)

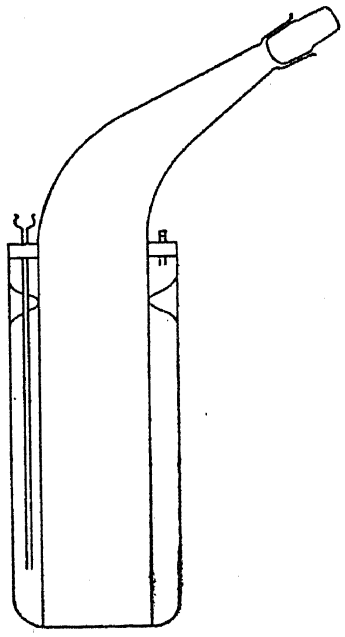


FIG. 1.

spectrograms were measured as usual and the results are tabulated in Tables I and II. The photographs are also reproduced in the accompanying plates. Dioxane was comparatively a poor scattering medium and an exposure of forty hours was required to bring out all the lines in its spectrum without any filter. Tetralin gave an intense picture at an exposure of nine hours ; but in this case a continuous spectrum was also present.

3. *Discussion of Results.*

(*a*) *Dioxane.*—Except for a short report on the principal Raman lines by Villars,[2] this compound has not been studied in any great detail. From the point of view of the Raman effect this is an interesting compound, for it affords the unique example of a molecule possessing a structure similar

2 Villars, *Jour. Amer. Chem. Soc.*, 1930, **52**, 4612.

to that of cyclohexane, but with two of the methylene groups replaced by oxygen atoms. As can be seen from the first column in Table III, the spectrum of dioxane consists of twenty-four lines of which fourteen have been observed for the first time. The author has been fortunate to be able to examine the cyclohexane plate of Krishnamurti[3] side by side with the latter and the comparison of the two reveals the following facts :—

(1) Both the compounds give only feeble wings accompanying the Rayleigh lines.

(2) All the important lines of cyclohexane appear more or less in the same position in dioxane.

(3) The region between 2863 and 2968 is covered by a band in both the cases which is attributed to the rotational spectrum accompanying the vibrational line due to C-H linkage.

(4) The wing structure of 1444 of cyclohexane is resolved into a close companion line in dioxane.

The outstanding differences in the two spectra are the following :—

(1) An intense line at 1306 (marked by the arrow in the accompanying plate) which is absent in cyclohexane, is one of the fundamental lines in dioxane and this is to be attributed to the oscillation of the group O $\langle^{CH_2}_{CH_2}$.

(2) The line due to the symmetrical oscillation of the carbons in cyclohexane at 804 is shifted to a higher frequency 837 in dioxane, and the lines due to C-H from 2852 and 2938 to 2863 and 2968 respectively.

(3) All the other lines belonging to C-C or CH_2 are shifted in the opposite direction.

(4) The line at 425 which is assumed to be one of the characteristic lines of the cyclohexane nucleus, is resolved into three lines in dioxane.

(5) There is a group of lines present in dioxane at about 2750 which is not present in cyclohexane and they may be explained partly as arising from the combination of 1444 and 1306.

(6) The intense doublet due to $C=H_2$ in cyclohexane at 2922 and 2938 appears as a single broad line at 2968 in dioxane.

It is clear from the above that dioxane possesses a structure similar to that of cyclohexane and its vibrations are modified to some extent by the presence of the two oxygen atoms in the place of two CH_2 groups in the ring.

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[3] Krishnamurti, P., *Ind. Jour. Phys.*, 1932, **6**, 543.

The presence of a weak line at 3064 which is characteristic of the aromatic linkage shows besides that it represents the transition between the aromatic and the aliphatic ring compounds.

(*b*) *Tetralin.*—This has been studied in great detail first by Bonino and Cella[4] and quite recently by Mukerji.[5] These authors have pointed out the great similarity of its spectrum to those of cyclohexane and naphthalene. The results given by them are in fair agreement with those of the author. As can be seen from Table III new lines have been observed at 268, 439, 459, 800, 905, 980, 1063, 1122, 1232, 2902 and 3008. The frequency shifts of cyclohexane and of benzene[6] are also given for comparison. The new points that have been observed by the author in the spectrum of tetralin besides those reported by the previous investigators, are the following :—

(1) The line at 1440 due to the deformation oscillation of CH_2 has been shifted slightly to a shorter wavelength and has been followed by a companion as in dioxane.

(2) The line at 425 has been split up into three lines as in dioxane.

(3) The continuous spectrum between 2865 and 2937 in cyclohexane and dioxane is present weakly also in tetralin and thus appears to be characteristic of the molecules of the cyclohexane type.

(4) The wings accompanying the Rayleigh lines are as prominent as in benzene.

(5) The important lines in the benzene spectrum at about 1600 due to C=C and above 3000 due to the aromatic CH appear also in tetralin.

(6) The line at 3046 shows a prominent wing on either side.

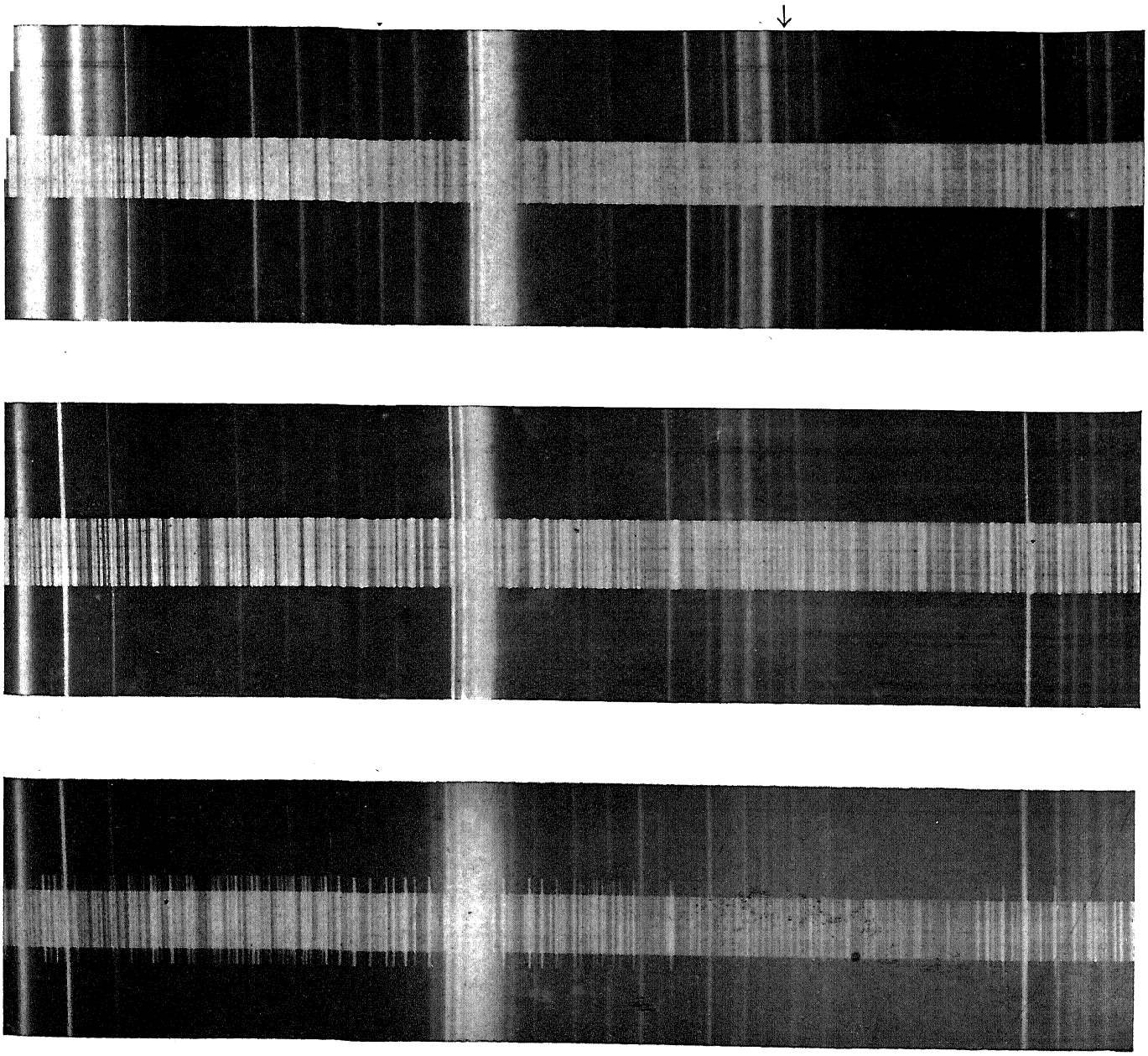
This similarity to the spectrum of cyclohexane on the one hand and of benzene on the other suggests that the molecule of tetralin is made up of one completed cyclohexane nucleus and one incomplete benzene nucleus.

In conclusion the author wishes to record his thanks to Sir C. V. Raman for his interest in the work.

Summary.

The Raman spectra of dioxane and tetralin have been obtained using the filter technique. The spectrum of dioxane consists of twenty-four lines of which fourteen are reported for the first time and resembles closely that of cyclohexane. Tetralin has also given eleven new lines. The results obtained are discussed with reference to the structure of the molecules.

4 Bonino and Cella, *Atti. Acad. Lincei*, 1931, 13, 784; also 1932, 15, 572.
5 Mukerji, *Phil. Mag.*, 1935, 19, 1079.
6 Grassman and Weiler, *Zeit. fur Phys.*, 1933, 86, 314.



I. Dioxane without filter. **II.** Dioxane with *o*-cresolthalin filter.
III. Tetralin with *p*-nitrotoluene filter.

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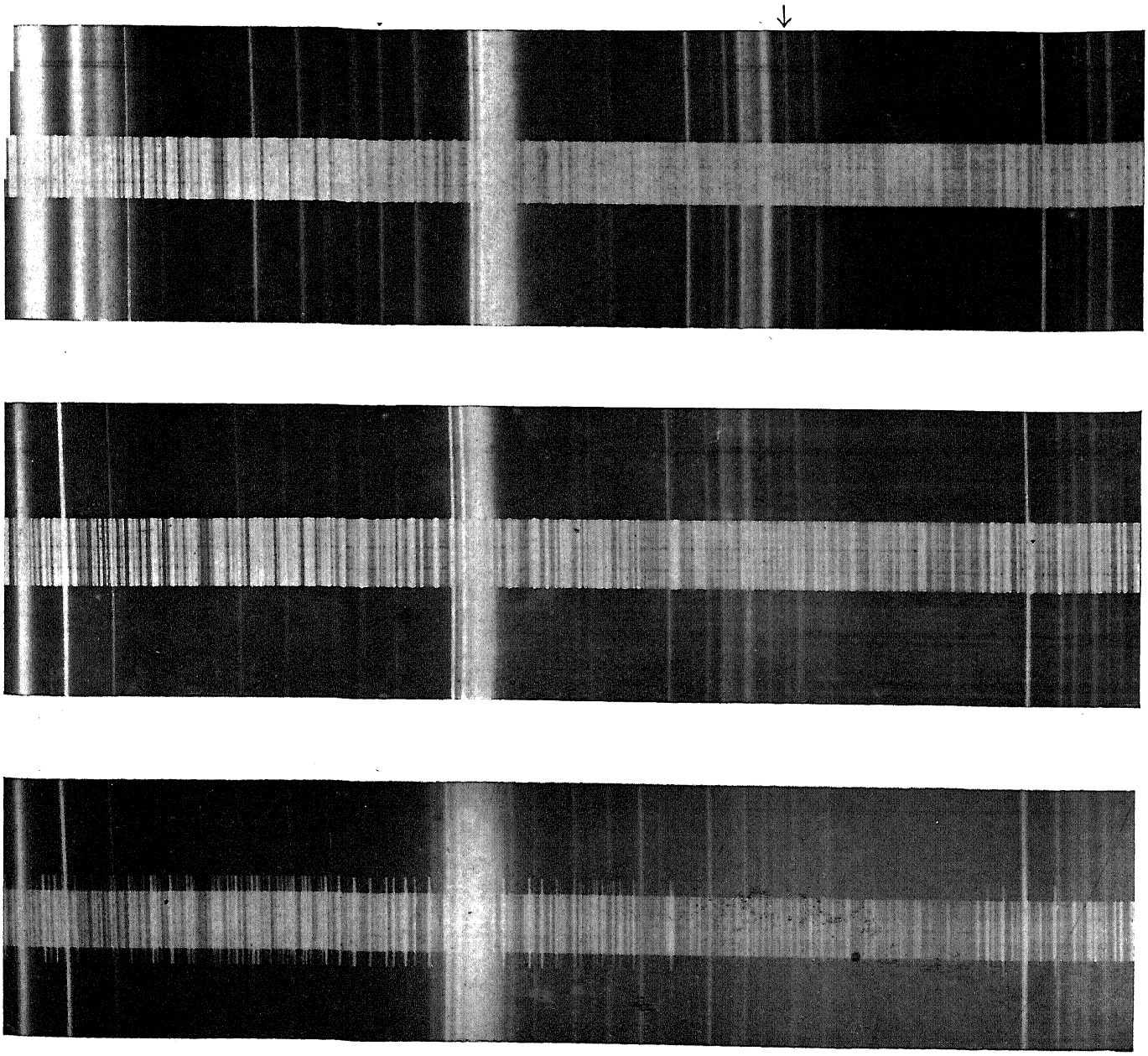

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