CCCXVI.—*Tesla-luminescence Spectra. Part VII. Some Aromatic Aldehydes.*

By ALFRED RUSSELL and ALFRED WALTER STEWART.

IN continuation of the investigation of the Tesla-luminescence spectra of organic compounds, the results obtained from a series of 20 aromatic aldehydes are now described. In an earlier investigation (J., 1923, **123**, 2145) the spectrum of benzaldehyde was found to consist of a peculiar series of bands in the visible region, to which the name " blue bands " was given for convenience; at the same time the normal emission in the benzenoid region (λ 2600—λ 3500) was completely extinguished. The same peculiarity has been observed in all the cases described below in which there is any emission which can be photographed; so evidently the aldehyde radical and the blue band emission are closely inter-related. It is rather surprising, however, to find that out of 17 aldehydes containing a single benzene nucleus in the molecule, no fewer than 11 show no detectable emission. This indicates how very markedly the Tesla-luminescence spectra are influenced by the introduction of substituent groups into the parent nucleus.

No emission spectra were yielded by the following substances: 2-methyl- and 2 : 4-dimethyl-benzaldehydes, β-phenylpropaldehyde,* salicylaldehyde, 3- and 4-hydroxybenzaldehydes, 2 : 4-dihydroxybenzaldehyde, protocatechuic aldehyde, 2-methoxybenzaldehyde,

* This aldehyde yields a spectrum containing the blue band series, but this emission appears to be due merely to an oxidation of the β-phenylpropaldehyde to benzaldehyde. When air is rigidly excluded during the experiment, no blue bands appear; but they can be produced by admitting air into the apparatus.

vanillin, 2-hydroxy-5-methylbenzaldehyde, citronellal, citral, and β-naphthaldehyde.

Benzaldehyde. The benzaldehyde bands present difficulties in measurement partly on account of the faintness of some of them and partly owing to the diffuseness of portions of the spectrum. A fresh examination of the spectrum by one of us (A. R.) led to the following determinations (wave-lengths, in Å.U.).

Group IV.	Group III.	Group II.	Group I.	Group 0.
—	4590	4230	3940	—
4972	4605—4615	4255—4275	3970—3980	3708
—	4650	4305	4010	—
—	4696—4726	4330—4370	4035—4070	—
—	4771	4410—4430	4090—4115	3849
—	4817	4450	4140	—
—	4852	4490	4170	3890
—	—	—	—	—
—	—	—	4205	3918

The wave-numbers per mm. of these 27 bands fall into a regular arrangement as shown in the following table, wherein the differences are indicated by italic numbers.

Group	0.		I.		II.		III.		IV.
Type of band.									
Strong	—		2538	*174*	2364	*185*	2179		—
Very strong, broad	2697	*181*	2516	*172*	2344	*175*	2169	*158*	2011
Strong	—		2494	*171*	2323	*172*	2151		—
Broad, faint	—		2468	*169*	2299	*176*	2123		—
Broad, faint	2598	*161*	2437	*175*	2262	*176*	2096		—
Sharp, narrow	—		2415	*168*	2247	*171*	2076		—
Sharp, narrow	2571	*171*	2398	*171*	2227	*166*	2061		—
Missing series	—		—		—		—		—
Faint	2553	*175*	2378		—		—		—

Considering the great difficulty in measuring the positions of the fainter and more diffuse bands, the regularity here is as good as can be expected.

3-*Methylbenzaldehyde.* The blue series of bands makes its appearance in the spectrum of this compound, but only 19 bands have been detected instead of the full 27. The wave-lengths are as follows :

Group IV.	Group III.	Group II.	Group I.	Group 0.
—	4577	4253	3949	—
4957—4977	4587—4607	4260—4270	3967—3977	3705
—	4649	4308	4003	—
—	—	—	—	—
—	4731	4377	4069	—
—	—	—	4135	—
—	—	4487	4156	—
—	—	4508	4207	—

When the wave-numbers of these bands are substituted for the wave-lengths, it becomes evident that there is a parallelism between this spectrum and that of benzaldehyde, thus :

Bands. Group	0.		I.		II.		III.		IV.
Strong	—		2532	*181*	2351	*166*	2185		—
Very strong	2699	*181*	2518	*174*	2344	*168*	2176	*163*	2013
Strong	—		2498	*176*	2322	*171*	2151		—
Missing series	—		—		—		—		—
Faint	—		2458	*174*	2284	*171*	2113		—
Faint	—		2418		—		—		—
Faint	—		2407	*179*	2228		—		—
Very faint	—		2377	*159*	2218		—		—

4-*Methylbenzaldehyde.* The spectrum of this compound contains only seven bands, which occur at λλ 4561—4571, 4230—4245, 3943—3958, 4360, 4400, 4080, 4120. When these are grouped according to wave-numbers, as in the following table, it is found that they correspond to similar bands in the benzaldehyde spectrum, although there is a definite shift of the whole series towards the end of shorter wave-length. The spectrum of 4-methylbenzaldehyde is much fainter than that of the parent substance.

Bands. Group	I.		II.		III.
Strong	2531	*171*	2360	*170*	2190
Missing series	—		—		—
Missing series	—		—		—
Faint	—		2294		—
Sharp narrow	2451	*177*	2273		—
Sharp narrow	2427		—		—

3 : 4-*Dimethylbenzaldehyde.* Here again the spectrum contains only bands belonging to the blue series, but there are three bands instead of 27, and the intensity of the emission is only moderate. The bands occur at λλ 4525—4545, 4215—4245, 3925—3955. Arranged according to wave-numbers, these positions are approximately 2538, 2364, 2206, from which it appears that the bands belong to Series I, II, and III.

4-*Propylbenzaldehyde.* In the spectrum of this compound four bands appear at the positions approximately indicated by the wave-lengths 4547—4575, 4232—4250, 3940—3960, 3700. By taking wave-numbers, the following arrangement is obtained :

Group	0.		I.		II.		III.
	2703	*171*	2532	*175*	2357	*164*	2193

These bands appear to correspond to some of the bands in the benzaldehyde spectrum, but (as in the case of 4-methylbenzaldehyde) the whole series is shifted towards the end of shorter wave-length.

Anisaldehyde. In the spectrum of this compound the three most prominent members of the blue series were present, although rather faint and indistinct. The approximate positions of the band heads are at λλ 3910, 4155, 4490, so they are roughly 100 units nearer the end of shorter wave-length than the corresponding bands of the parent benzaldehyde.

Piperonal. An examination of this substance revealed a faint greenish-blue glow, but no photographic record of the spectrum could be obtained.

Discussion.—From the foregoing results it seems possible to draw the following inferences.

1. When a compound containing the aldehyde group yields a Tesla-luminescence spectrum, the emission is in the blue region. Since acetaldehyde shows emission between λλ 3650 and 4750, and propaldehyde between 3400 and 4850, it seems evident that the spectrum in the blue region is characteristic of the group ·CHO. Further, the banding of these spectra is confined to the benzene derivatives, which seems to indicate that the bands have their origin in the phenyl nucleus as altered by the influence of the aldehyde radical.

2. In the case of the aromatic aldehydes, it appears that the presence of a methyl group in the ortho-position to the aldehyde radical has the effect of extinguishing the emission in the blue region. Neither 2-methyl- nor 2 : 4-dimethyl-benzaldehyde shows any sign of emission.

3. When a methyl group is inserted in either the meta- or the para-position with respect to the aldehyde group (or if both these positions are simultaneously occupied by methyl groups), it is possible to find emission in the blue region; but the effect of the substitution is marked by a change in the number of bands which can be detected in the spectrum, as the following figures show :

Benzaldehyde	27 bands	4-Propylbenzaldehyde	4 bands
3-Methylbenzaldehyde ...	19 ,,	3 : 4-Dimethylbenzaldehyde	3 ,,
4- ,, ,, ...	7 ,,		

Further, the introduction of alkyl groups in the meta- or the para-position with respect to the aldehyde group tends to shift the spectrum as a whole towards the end of shorter wave-length as compared with the corresponding benzaldehyde spectrum. This is illustrated by the following figures, showing the position of the strongest bands in the spectra of benzaldehyde and of 3- and 4-methylbenzaldehyde. 4-Propylbenzaldehyde gives similar results.

Group	IV.	III.	II.	I.	0.
Benzaldehyde	4972	4605—4615	4255—4275	3970—3980	3708
3-Methylbenzaldehyde ...	4957—4977	4587—4607	4260—4270	3967—3977	3705
4-Methylbenzaldehyde ...	—	4561—4571	4230—4245	3943—3958	—

This shift of the spectrum towards the short-wave end seems likely to be of considerable importance when the theory of the Tesla-luminescence spectra is developed; for it places these spectra in a category entirely apart from absorption spectra. In the latter an increase in molecular weight without alteration of the chemical character of the molecule (*i.e.*, by the introduction of methyl groups) tends to shift the spectrum towards the visible region; whereas in the cases just quoted, the exchange of a hydrogen atom for a methyl radical produces exactly the opposite effect and shifts the spectrum as a whole towards the ultra-violet.

4. The introduction of two alkyl groups does not prevent the emission of a spectrum, provided that neither of the alkyl radicals is in the ortho-position to the aldehyde group. Thus 3 : 4-dimethylbenzaldehyde yields a spectrum, but the 2 : 4-isomeride shows no emission.

5. The introduction of the hydroxyl group in any position in the benzaldehyde nucleus appears to prevent the emission of the normal spectrum. Thus no emission was detected in any of the following cases: salicylaldehyde, 3- and 4-hydroxybenzaldehydes, 2 : 4-dihydroxybenzaldehyde, protocatechuic aldehyde, and 2-hydroxy-5-methylbenzaldehyde.

6. The methoxy-group appears to differ from its parent hydroxyl in its influence. Thus 2-methoxybenzaldehyde, like salicylaldehyde, shows no emissive power, nor does vanillin (although in this case the free hydroxyl group may be the inhibiting factor); but anisaldehyde, which contains the methoxy-group in a position para to the aldehyde radical, shows emission. This spectrum of anisaldehyde is of peculiar interest, since it has a most striking resemblance to that of acetophenone. In both cases the sharp banding of benzaldehyde is replaced by a continuous spectrum in the same region with three bright centres of emission corresponding to the bright banded parts of the benzaldehyde spectrum; and in each case the points of maximum emission are shifted towards the ultra-violet end of the scale (as compared with benzaldehyde) to almost the same extent: in acetophenone the aldehydic hydrogen atom has been replaced by a methyl group, whereas in anisaldehyde it is the para-hydrogen atom which has been replaced by the methoxy-group.

The striking resemblance between the spectra of acetophenone and anisaldehyde is noticed at once when the plates are compared; and it is in marked contrast to the difference between the spectra of the two similarly constituted 4-methyl- and 4-methoxy-benzaldehydes, for the former shows clear banding which is not perceptible in the spectrum of the latter. In these cases, evidently, position isomerism sinks into a subsidiary place in comparison with the chemical character of the substituent.

7. The methylene ether, piperonal, occupies a somewhat doubtful

position. By analogy with its parent protocatechuic aldehyde, it should yield no emission, but actually a faint greenish-blue glow was detected visually, which seems to indicate that it emits in the blue region.

8. It appears that the intensities of the various spectra are affected by the mass and also by the number of substituents present. Thus 4-methyl- and 4-propyl-benzaldehydes emit almost identical spectra, but the spectrum of the latter is much feebler than that of the 3-methyl derivative. Further, the spectrum of 3 : 4-dimethylbenzaldehyde is weaker than those of 3- and 4-methylbenzaldehyde.

9. Up to the present, in this investigation two groups, and two only, have been detected as capable of forming centres of emission under the Tesla discharge, *viz.*, the benzene ring and the carbonyl radical. In the series of substances now described, these two foci of emission are combined in a single molecule, and it is of importance to find that they result in the complete blotting out of the normal benzene emission and in an emission in the normal carbonyl group region of the spectrum with the production of a banded spectrum instead of the continuous emission observed among the aliphatic aldehydes and ketones.

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THE SIR DONALD CURRIE LABORATORIES,
THE QUEEN'S UNIVERSITY OF BELFAST. [*Received, July 27th,* 1929.]