CCCXIX.—*Tesla-luminescence Spectra. Part VIII. Some Halogen-substituted Derivatives of Benzene.*

By Alfred Russell and Alfred Walter Stewart.

It has previously been reported that no light emission could be detected when chlorobenzene vapour was excited by the high-tension discharge from a Tesla transformer (J., 1923, **123**, 2155). A careful re-examination of chlorobenzene has shown, however, that it does give a feeble emission consisting of 12 sharp narrow bands between λ 2955 and λ 2745. As would be expected, fluorobenzene gives a much more complete spectrum than chlorobenzene, there being at least 45 sharp bands extending from λ 3425 to λ 2578; moreover, both spectra are in the same region and differ only in intensity, that of chlorobenzene being much fainter, and both fade

towards the red end, the ultra-violet limit being sharp. This sharp ending is evidently due to absorption, since by diluting the vapours with alcohol vapour and so reducing the amount of absorption, it was possible to measure a number of additional bands that did not appear when the pure vapours were used. No light emission at all has been detected in the cases of bromobenzene and iodobenzene. Both *o*- and *p*-dichlorobenzene gave spectra in the green region as well as in the ultra-violet. *m*-Dichlorobenzene only gave a feeble emission in the green that could not be photographed. The chlorotoluenes and *p*-fluorotoluene all give both ultra-violet spectra and very intense spectra in the green region.

The presence of a halogen atom in the ring, as in the cases of *p*-chloroacetophenone, the chloroanilines, and the chlorophenols, has only a weakening effect, the spectra being merely those of the parent substances but containing fewer bands, except in the case of phenol and *o*-chlorophenol. In the spectrum of phenol six bands have been measured (J., 1923, **123**, 2854); *o*-chlorophenol gives a faint spectrum containing 14 bands, of which 5 coincide with bands in the spectrum of phenol, the other phenolic band being missing. The spectrum of *p*-chlorophenol is a continuation of that of phenol towards the visible region, and its bands coincide with bands in the spectrum of the *o*-chloro-compound.

In all the banded spectra obtained, it has been found that a simple wave-number relationship holds between the bands, the series of bands, for any one compound, being divisible into groups, the members of which exhibit a constant difference from their congeners in the other groups. It has also been established that where a compound gives a green in addition to an ultra-violet spectrum, the bands in the green fall into the same series as those in the ultra-violet, congeners showing a constant difference from one another. From this it seems that the green spectrum, when it is obtained, is merely the projection of the ultra-violet spectrum through a definite interval.

The point is made clear by comparing the wave-numbers per mm. of the green and ultra-violet spectra of *p*-chlorotoluene :

Bands in u.-v. spectrum	3514	3505	3460	3435	3426	3353
Bands in visible spectrum	2174	2166	2120	2098	2083	2020
Differences	1340	1339	1340	1337	1343	1333

Corresponding bands in the groups, either in the ultra-violet or the green, differ by ν 80, and the bands in the green differ from their congeners in the ultra-violet by ν 1340. For *p*-xylene the corresponding differences are ν 83 and ν 1320. For *p*-fluorotoluene the differences are the same as for the *p*-chloro-compound.

Experimental Results.—Wave-numbers only of the bands are given, and the bands, in each case, are arranged in groups, the differences between corresponding bands being given in parentheses.

Chlorobenzene. This gave a faint spectrum consisting of 12 sharp narrow bands arranged in pairs, the difference between corresponding bands being ν 104.

Group 1.		2.		3.
3643	(103)	3540	(101)	3439
3635	(102)	3533	(103)	3430
3603	(106)	3497	(105)	3392
3594	(106)	3488	(104)	3384

Fluorobenzene. An intense spectrum was obtained between λ 2578 and λ 3425 with bands measured at the following positions (those marked with an asterisk appeared only on diluting the vapour with alcohol vapour).

Group. 1.		2.		3.		4.		5.		6.	7.
—		3796*	(97)	3699	(101)	3598	(102)	3496	(102)	3394	—
—		3791*	(96)	3695	(105)	3590			(300)		3290
3883*	(102)	3781	(100)	3681	(104)	3577	(100)	3477	(102)	3375	—
3871*	(100)	3771	(99)	3672	(101)	3571		—		—	—
3865*	(97)	3768		—		—		—		—	—
3858*	(97)	3761	(105)	3656	(102)	3554	(99)	3455		—	—
3852*	(100)	3752	(101)	3651	(102)	3549		—		—	—
3839*	(100)	3739	(103)	3636	(101)	3535	(102)	3433	(102)	3331	—
—		3727	(99)	3628	(99)	3529		—		—	—
3821*	(100)	3721	(105)	3616	(102)	3514	(101)	3413	(104)	3309	—

The difference between corresponding bands is nearly ν 100.

o-*Dichlorobenzene.* This compound gave a visible green spectrum, which could not be photographed, and a spectrum in the ultra-violet between λ 2915 and λ 3310 containing six indistinct bands.

Group 1.		2.		3.
3492	(108)	3384	(108)	3276
3461	(110)	3351	(107)	3244

The wave-number difference between corresponding bands is ν 108.

m-*Dichlorobenzene.* A faint visible green spectrum was obtained, which could not be photographed, but no ultra-violet spectrum.

p-*Dichlorobenzene.* This gave a visible green spectrum, which could not be photographed, and a spectrum in the ultra-violet between λ 2915 and λ 3310. In the latter, 8 bands were measured, 6 of them being identical with the bands in the spectrum of the *o*-compound.

Group 1.		2.		3.		4.
—		3491	(107)	3384	(108)	3276
3570	(110)	3460	(109)	3351	(107)	3244
3540		—		—		—

The wave-number difference between corresponding bands is ν 108.

o-*Chlorotoluene*. The strong banded spectrum in the visible has been photographed between λ 4606 and λ 4951, but extends continuously to the red limit; there is also an ultra-violet spectrum between λ 2808 and λ 3400. Bands are measured as follows: visible, λλ 2157, 2093; ultra-violet, 3551 and 3544.

m-*Chlorotoluene*. A fairly intense continuous spectrum in the ultra-violet between λ 2773 and λ 3356 appears to be accompanied by a faint green spectrum, which was not photographed.

p-*Chlorotoluene*. An intense spectrum in the visible extending to the red limit was photographed between λ 4600 and λ 4951 with bands at the following positions:

Group	1.		2.		3.
	2174	(76)	2098	(78)	2020
	2166	(83)	2083		—
	2120		—		—

The difference between corresponding bands appears to be ν 80, the large variation being accounted for by the breadth of the bands.

In the ultra-violet there is an intense banded spectrum between λ 2823 and λ 3535:

Group	1.		2.		3.
	3514	(79)	3435	(82)	3353
	3505	(79)	3426		—
	3479	(79)	—	(79)	3321
	3460		—		—

The wave-number difference between corresponding bands is ν 80.

p-*Fluorotoluene*. An intense visible spectrum extending from the green to the red limit had bands as follows:

Group 1	2151	2131	2122	2102
Group 2	2068	—	—	2026
Difference	83	—	—	76

The wave-number difference appears to be 80, but the breadth of the bands renders the values somewhat uncertain.

There is, in addition, an intense, well-banded, ultra-violet spectrum extending from λ 2657 to λ 4115:

Group	1.		2.		3.		4.
	3655	(82)	3573	(83)	3490		—
	3641	(79)	3562	(84)	3478		—
	3635	(80)	3555	(83)	3482	(81)	3391
	—		3536		—		—
	3602	(86)	3516	(79)	3437		—
	3593	(82)	3511	(81)	3430		—
	3580	(80)	—	(81)	—	(81)	3338

The wave-number difference between corresponding bands appears to be 81·5.

o-*Chlorophenol*. A faint ultra-violet spectrum had broad bands

which were measured at the following positions (the mean between the edges of a band has been taken as its position).

Group	1.		2.		3.		4.
	—		—		3385	(104)	3281
	—		—		3369	(109)	3260
	—		3446	(98)	3348		—
	3528	(99)	3429	(100)	3329	(106)	3235
	3507	(100)	3407	(103)	3304	(105)	3199

p-*Chlorophenol.* A faint ultra-violet spectrum between λ 2930 and λ 3750 had diffuse bands at λλ 3394, 3369, 3355, 3328, 3310, 3413, the mean of the two edges of a band being taken as its position.

Chloroanilines. The isomeric monochloroanilines all give similar spectra that appear to be just the aniline spectrum modified by the presence of the halogen atom in the ring. All three give faint continuous spectra with no lines or bands, the approximate limits being given together with those of the aniline spectrum for comparison.

o-Chloroaniline.	*m*-Chloroaniline.	*p*-Chloroaniline.	Aniline.
3175—3515	3005—3758	3098—3844	2982—3875

The spectrum of aniline is much more intense than those of the chloroanilines. *p*-Chloroaniline gives the most intense spectrum of the three halogen-substituted products, that of the *o*-isomeride being the weakest.

THE SIR DONALD CURRIE LABORATORIES,
THE QUEEN'S UNIVERSITY OF BELFAST. [*Received, July 30th*, 1929.]