CCCXV.—*Tesla-luminescence Spectra. Part VI. Some Phenolic Compounds and their Ethers.*

By James Cameron Macmaster, Alfred Russell, and Alfred Walter Stewart.

In previous papers (J., 1923, **123**, 642, 817, 2147; 1924, **125**, 1743; 1925, **127**, 999) accounts were given of the spectra emitted under the Tesla discharge by the vapours of a number of organic compounds. The present communication describes the results obtained with the same apparatus when used to examine certain hydroxy-compounds and their ethers. The figures given are wave-lengths (Å.U.), except when otherwise stated. For photographs of the spectra in general, Imperial Eclipse plates were used and an exposure of 30 minutes was given. Where emission occurred in the visible region, further photographing was done with the aid of Imperial Panchromatic plates with double the exposure. The slit aperture of the spectrograph was 0·125 mm.

The general results obtained may be seen in the table below. In the column headed "Cont. emiss." the limits of the continuous spectrum of each substance are given; and under "Max." a note is made of the regions of greatest brilliancy. The occurrence of a glow in the visible region of the spectrum is indicated by means of a + in the column headed "Vis." When any bands were observed, their positions have been noted in the last column, those wave-lengths in parentheses being apparently close doublets.

Substance.	Cont. emiss.	Max.	Vis.	Bands.
Phenol	2770—3660	3050	0	2735, 2747, (2761, 2767), 2773, 2782, (2811, 2815), 2828, (2847, 2853), 2883, 2897, 2916, 2936, 2955, 2989, 3011, 3029, 3046 ?
Anisole	2850—4500	3270	0	None
Phenetole	2741—3710	3000	0	2791, 2809, 2823, 2846, 2884, 2894, 2913, 2933
o-Cresol	2770—3700	2900—3000	0	None
m-Cresol	2760—3750	2900—2950	0	None
p-Cresol	2830—3600	3000	+	2834, 2854, 2872, 2890, 2904, 2921, 2939, 2976, 2999, 3014, 3035, 3075, 3091, 3131, 3172, 4790
o-Tolyl methyl ether	2730—3800	3000	+	2749, 2766, 2793, 2810, 2824
p-Tolyl methyl ether	2825—3600	3000	0	2826, 2847, (2870, 2875), (2893, 2898), 2915, 2937, 2968, 3009, 3042, 3073
4-*m*-Xylenol	2810—3850	3050	+	None
4-*o*-Xylenol	2830—3500	3040	+	None
3-*p*-Xylenol	2780—3600	2940	+	None
Carvacrol	2800—3400	3000	0	None
ψ-Cumenol	2820—3700	3050	0	None
Anethole	2980—4300	3300	+	3145, 3190
Pyrocatechol	No spectrum			
Resorcinol	2750—3520	2980	0	(2761, 2766), (2781, 2787), 2803, 2822, (2841, 2846), (2861, 2866), 2885, (2903, 2908), (2924, 2928), 2947, 2973, 3000
Quinol	2920—3900	3180	+	2840, 2849, 2869, 2900, 2916, 2937, 2947, 2973, 2989, 3012, 3028, 3052, 3083, 3109, 3153 3192, 3236, 3274
Guaiacol	2790—3900	3050	+	None
Veratrole	2870—3900	3050	+	None
Resorcinol monomethyl ether	2820—3500	3050*	0	None
Resorcinol dimethyl ether...	2761—4300	3000†	0	(2765, 2769), 2794, 2826, 2837, 2910
Quinol monomethyl ether ...	2900—4100	3170	0	2827, 2867, 2936, 2969, 2977, 3022, 3055, 3094, 3129, 3180
Quinol dimethyl ether	2880—4200	3200	0	2954, 2971, 2999, 3031, 3049
Orcinol	2800—3400	3000	0	None
Orcinol monomethyl ether	No spectrum			
Orcinol dimethyl ether	2780—3700	2990	0	None

* There is a sudden increase in brightness at 2915.
† There is a sudden increase in brightness at 2910.

Substance.	Cont. emiss.	Max.	Vis.	Bands.
Eugenol	2830—4000	3150	+	None
Safrole	2930—3950	3200	+	None
*iso*Safrole	3060—4000	3450	+	None
Phloroglucinol	No ultra-violet spectrum		+	None
Pyrogallol	No ultra-violet spectrum		+	None
Phloroglucinol triethyl ether	4010—4800	4500	0	None
Pyrogallol trimethyl ether	No spectrum			
Diphenyl ether	2750—3550	2950—3050	0	None
Benzyl methyl ether	2706—3241	—	+	2706—2745, 2788—2820, 2864—2909, 2963—3037
Benzyl ethyl ether	2658—3332	—	+	2712, 2726, 2787, 2805, 2851—2905, 2952—3016, 3065, 3093, 3126, 3161
α-Naphthol	3120—4300	3450	+	3179, 3235, 3340, 3484
β-Naphthol	3150—4900	3450	+	3238, 3300, 3395
α-Naphthyl ethyl ether	3060—4250	3400	+	3164, 3320,3480, 3660
β-Naphthyl ethyl ether	3150—4300	3500	+	3229, 3300, 3390
Tetrahydro-α-naphthol	3180—3700	3350	+	None

The following table gives the results observed in the visible region of the spectrum.

p-Cresol	Slight green glow, leaving no trace on Panchromatic plate. Direct-vision spectroscope shows one band head at 4790 degrading towards red.
o-Tolyl methyl ether	Slight greenish glow unresolved by direct-vision spectroscope.
The three xylenols	Weak unresolvable green glow.
Anethole	Continuous spectrum extends up to visible.
Quinol	Weak green glow, unresolvable.
Guaiacol and veratrole	Fairly strong deep violet glow.
Eugenol, safrole, *iso*safrole	Deep violet glow.
Phloroglucinol and pyrogallol	Slight green glow.
Benzyl methyl ether	The complete series of blue bands was measured.
Benzyl ethyl ether	,, ,, ,, ,, ,,
α- and β-Naphthol	Very strong deep violet glow.
The two naphthyl ethers	,, ,, ,, ,,
Tetrahydro-α-naphthol	Very weak green glow.

Discussion.

In considering the results obtained by comparing the wave-numbers per mm. of the various bands observed, it is found that in some of the spectra examined there appear to be band systems which manifest certain regularities in their grouping. Some examples of these are tabulated below.

Phenol.

3656	3554	3451	3345
3641	3536	3429	3323
3622	3512	3406	3301

The average difference between the values on the same horizontal line is 105 units. The phenetole bands can be grouped into an approximately similar series.

p-*Cresol.*

(I)	3529	3483	3443	3401	3360	3318	3276	3235	3194	3153
(II)	3504	3460	3424	?	3334	3295	3252			

The bands in this spectrum can be arranged in two groups with a constant difference of about 42 units in wave-number between adjacent members of a group.

A somewhat similar grouping can be traced in the spectrum of *p*-tolyl methyl ether; and the spectra of resorcinol and quinol can also be resolved into two series of bands, although here the constancy of the differences is less satisfactory.

The influence of substitution upon the spectra may now be considered, and obviously it has three aspects: (*a*) the general effect of loading the benzene ring; (*b*) the influence of position isomerism; and (*c*) the result of replacing the hydroxylic hydrogen atoms by alkyl groups.

Unless a substituent is introduced para to the hydroxyl group, the general effect of loading the nucleus is similar to that already observed in other cases. The weighting of the ring appears to damp down the vibrations which give rise to the benzene bands, with the result that the emission becomes continuous.

A *p*-substituent appears to exert an influence different from that of an *o*- or *m*-substituent. Thus para-substitution tends to extend the general emission towards the red end of the spectrum to an extra 50 units of wave-length. Where there are only two substituents in the nucleus (one of which is the hydroxyl radical) a new series of bands makes its appearance when the substituents are in the para-position; and in several cases two such series appear simultaneously and overlap each other. The difference in wave-number between the separate bands of each group is about 43 units. These bands appear when the second substituent is an alkyl group or a hydroxyl radical, and they seem to be characteristic of para-substituted phenolic compounds containing no other substituents. Resorcinol and its ethers give an analogous overlapping series; but in this case the band difference is about 50 units.

When the alkyl substituent replaces the hydroxylic hydrogen atom in the parent compound, the effect is in general to strengthen the emissive power. The only notable exceptions to this rule are orcinol monomethyl ether, diphenyl ether, and β-naphthyl ether. There seems to be no definite connexion between the nature of the substituent and the direction in which the spectrum is shifted.

An interesting and suggestive point concerning the ethers is found when their spectra are compared with those of corresponding chains composed entirely of hydrocarbon radicals. The resemblance between the spectra of ethylbenzene, $Ph{\cdot}CH_2{\cdot}CH_3$, and anisole, $Ph{\cdot}O{\cdot}CH_3$, is not very marked, although both are of the same intensity and they occur fairly near each other in the spectral range. A closer resemblance is noticeable between the spectra of diphenylmethane and diphenyl ether. Here both spectra begin at almost the same point at the ultra-violet end, they have comparable intensities, and the only marked difference between them is the fact that the diphenylmethane spectrum extends further towards the red :

Ph·CH$_2$·Ph	2673—3900
Ph·O·Ph	2750—3550

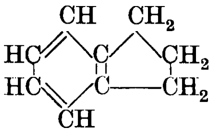
Obviously, both these molecules contain a mechanism capable of producing emission in the region 2750—3550; and in neither case does this mechanism seem capable of yielding individual bands.

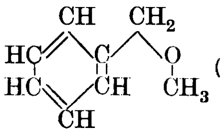
A much more striking parallelism is found when the spectra of hydrindene (I) and benzyl methyl ether (II) are compared. Here a fresh factor makes its appearance, for both compounds emit what may be termed interrupted spectra, *i.e.*, spectra characterised by a region of non-emission situated between two regions of emission.

	Banded emission.	Continuous emission to	Bands in visible region.
Hydrindene	2702—2803	3700	4584—5965
Benzyl methyl ether	2706—3037	3241	4203—4990

Complete identity in the measurements is not to be expected, and the resemblance in general character is quite sufficient to show that the two molecules contain analogous mechanisms. If the van 't Hoff tetrahedral model for the carbon atom be adopted, it will be found that the open chain of the ether will naturally bend itself in a curve, and the similarity of the two structures becomes apparent.

(I.)

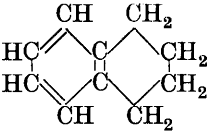


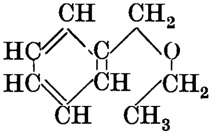


(II.)

The correctness of this assumption can be tested by a comparison between the spectra of tetrahydronaphthalene (III) and benzyl ethyl ether (IV). As can be seen from the formulæ, these two structures have a resemblance to each other which is parallel to that between hydrindene and benzyl methyl ether. Here again

(III.)





(IV.)

the two spectra are of the same type, for each contains (*a*) a banded region in the ultra-violet, (*b*) an extension of this region with only continuous emission, (*c*) a gap with no emission, and (*d*) a region of emission in the visible.

	Banded emission.	Continuous emission to	Bands in visible region.
Tetrahydronaphthalene	2719—3179	4400	4572—6170
Benzyl ethyl ether	2658—3161	3332	4203—4990

From the foregoing facts, it seems established that spatial relationships have a definite influence in some cases of Tesla-luminescence.

The case of α-naphthol and *ar*-tetrahydro-α-naphthol brings to light another interesting point. The emission of the former extends between λ 3120 and λ 4300, and in the visible region it yields a very strong violet glow. The latter emits a much shorter and fainter spectrum which begins at almost the same region (λ 3180) but extends only to λ 3700, whilst the violet is replaced by a green glow in the visible portion of the spectrum.

It is generally admitted that the naphthols do not contain a pair of normal benzene rings, whereas *ar*-tetrahydro-α-naphthol is a normal phenolic compound. Now the green glow phenomenon is observed in cases where a benzene ring carries two alkyl substituents in the ortho-position, as in *o*-xylene, or in which both ends of a hydrocarbon chain are attached to ortho-positions, as in tetrahydronaphthalene. It is therefore noteworthy that the abnormal α-naphthol yields a violet glow, whereas the normally phenolic nucleus of the tetrahydro-derivative, with its two ortho-substituents formed by the ends of the reduced chain, behaves as might be expected and yields the green glow.

Further, if the abnormal class of the naphthols be ignored, the violet glow has been observed up to the present only in the following cases: guaiacol, veratrole, eugenol, safrole, and *iso*safrole. In each of these compounds there is ortho-substitution and the atoms directly attached to the benzene ring are oxygen atoms.*

In some of the spectra described above, a band made its appearance at λ 4315. This is probably identical with a band at λ 4314 which is mentioned by Watts ("Index of Spectra," V, 69) as occurring in the spectrum of "carbon hydride." The band at λ 4315 has been observed in the Tesla-spectra of the following substances: pyrocatechol, guaiacol, veratrole, resorcinol monomethyl ether, resorcinol dimethyl ether, quinol mono- and di-methyl ethers, eugenol, phloroglucinol triethyl ether, pyrogallol trimethyl ether. In the cases of safrole and *iso*safrole a band was observed at λ 4310.

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* In the case of pyrogallol—which also fulfils the conditions—a green glow was faintly manifest; but as the main spectrum obtained from pyrogallol (and also from phloroglucinol) was a combination of the spectra of water and carbon monoxide, it is evident that no great weight can be attached to the observation.

It is evident that this band is found mainly among the spectra of the ethers, and the suggestion was made by one of us (J. C. M.) that it results from the decomposition of the ether with liberation of the alkyl group and the parent phenol. The simpler ethers are more stable than the complex, and so do not yield the band in their spectra.

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