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## Further Alkylbenzene Spectra to 1750A\*

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The absolute absorption intensities of *n*-butyl-, secondary butyl-, and tertiary butylbenzene and of 1,3,5-trimethylbenzene (mesitylene) have been measured to about 1750A. Increased branching of the side chain shifts the 1900A and 2100A bands slightly to shorter wave-lengths but increases the total oscillator strength from 1.04 for *n*-butyl to 1.57 for tertiary butyl. The wave-length shifts are in the same direction, the intensity changes in the opposite direction from those observed in the 2600A bands of these same compounds. The mesitylene spectrum is about 1000 cm<sup>-1</sup> to the red of the meta-xylene spectrum and its oscillator strength is reduced to 0.89, almost as low as that of benzene itself.

CONTINUING our earlier studies on alkylbenzene spectra in the far ultraviolet,<sup>1</sup> we have obtained the absorption curves of *n*-butyl-, secondary butyl-, and tertiary butylbenzene and of mesitylene to about 1750A in *n*-heptane solution in a 0.13 mm cell. The apparatus and techniques used were identical with those previously described. This is the first time absorption intensities have been measured below 2000A on these compounds, though the vapor spectrum of mesitylene in the 2000A-1000A region was obtained earlier in this laboratory.<sup>2</sup>

The compounds used here were Eastman Kodak Company samples which were purified by recrystallizing several times, then by distilling twice through a Podbielniak column of 50 equivalent plates, taking the center cut each time. The final constants were: mesitylene,  $n_D^{20}$  1.4985, b.p. 165°C; *n*-butylbenzene,  $n_D^{20}$  1.4890, b.p. 181°C; secondary butylbenzene,  $n_D^{20}$  1.4898, b.p. 173°C; tertiary butylbenzene,  $n_D^{20}$  1.4941, b.p. 169°C.

The spectra are qualitatively and quantitatively similar to those of the alkylbenzenes studied earlier, with a band of moderate intensity near 2100A and a strong allowed transition at shorter wave-lengths. The butylbenzene curves

are shown in the top half of Fig. 1. The mesitylene curve is in the bottom half together with earlier curves for benzene with 0, 1, and 2 alkyl substituents in the meta sequence for comparison. Some of the main features of the new curves are tabulated in Table I.

The *n*-butyl curve coincides with the earlier ethylbenzene curve within the experimental error of about 10 percent at every point, and the oscillator strengths or *f*-values obtained from the integrated areas under the curves differ by only

TABLE I. Main features of spectra of butylbenzenes and mesitylene.

	<i>n</i> -butyl	Secondary butyl	Tertiary butyl	Mesitylene
A. Forbidden transition				
Onset of absorption	2180A 45800 cm <sup>-1</sup>	2170 46100	2160 46300	2270 44000
Peaks of component bands	46700 47600 48600 49500(?)	47000 47800 48700 49700(?)	47000 47900 48800 49700	44800 45700 46600
$\epsilon_{\max}$	7000	10800	9300	9500
Approx. oscill. strength, <i>f'</i> of this transition (to arbitrary cut-off)	0.11 (2000A)	0.18 (1995)	0.16 (1985)	0.12 (2110)
B. Allowed transition				
Peak	1890A 52900 cm <sup>-1</sup>	1880 53100	1880 53200	1990 (double) 50300
$\epsilon_{\max}$	50000	70000	85000	46000
Components	51800 53000 54200(?) 55000(?)	52100 53100 54200(?)	52400 53300	49800 50900
Total oscill. strength, <i>f</i> of both transitions	1.04	1.37	1.57	0.89

\* This work was assisted by the Office of Naval Research under Task Order IX of Contract N6ori-20 with the University of Chicago.

<sup>1</sup> J. R. Platt and H. B. Klevens, Chem. Rev. **41**, 301 (1947).

<sup>2</sup> W. C. Price (unpublished).

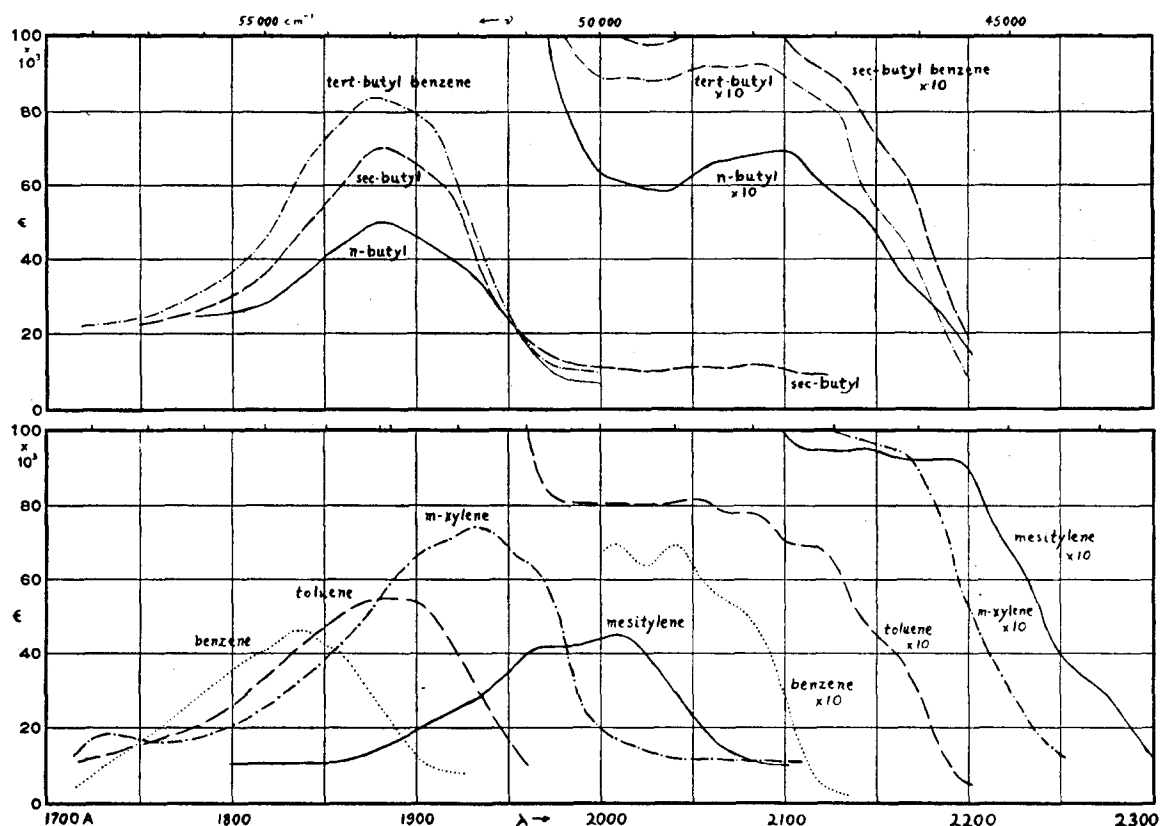


FIG. 1. Spectra of alkylbenzenes.

seven percent. This agreement supports the familiar rule that molar absorption is almost independent of the length of saturated side chains; and it therefore gives us some confidence in the consistency and reproducibility of our measurements.

The secondary butyl curve is shifted about  $250\text{ cm}^{-1}$ , and the tertiary butyl curve about  $350\text{ cm}^{-1}$  to shorter wave-lengths from the *n*-butyl curve. These shifts are in the same direction as the shifts observed in the  $2600\text{Å}$  bands of these same compounds<sup>3,4</sup> but are larger, a phenomenon which we have observed in several other benzene derivatives. The intensity changes, on the other hand, vary in the opposite direction from the intensity changes in the longer wave-length bands, the ratio of the *f* values of tertiary to

normal butyl being about 1.5 here, where in the  $2600\text{Å}$  bands the ratio is about 0.8.<sup>4</sup> Probably because of this crossover, the sequence is shuffled in the  $2100\text{Å}$  bands, with the secondary butyl curve lying above the other two in that region.

The crossover of intensities results in the curious fact that the  $2600\text{Å}$  bands in tertiary butylbenzene<sup>4</sup> are actually weaker relative to the  $1900\text{Å}$  bands, that is to say, *more forbidden*, than in benzene itself! This re-emphasizes the remark made earlier<sup>1</sup> that it is not merely loss of symmetry which causes the usual increase of intensity of the  $2600\text{Å}$  bands in substituted benzenes; for tertiary butylbenzene has quite low symmetry. The changes must evidently be understood in terms of specific electronic interactions of the substituent with the ring, which for some reason reduce the relative intensity in the present case.

Since the wave-length shift in the butylbenzenes is in the same direction as that observed in the  $2600\text{Å}$  bands, while the intensity change is in

<sup>3</sup> See, for example, F. A. Matsen, W. W. Robertson, and R. L. Chuoke, *Chem. Rev.* **41**, 273 (1947).

<sup>4</sup> American Petroleum Institute Research Project 44 at the National Bureau of Standards. Catalog of Ultraviolet Spectrograms. Sequences of curves from several laboratories.

the opposite direction, it follows that at least two parameters must be assigned even to alkyl substituents in order to account for the changes in the three benzene-like bands. The same conclusion might have been reached from inspection of intensities alone in the earlier xylene curves, where the 1900A benzene-toluene-o-xylene sequence was in the same order as in the 2600A bands, but the meta-para order of intensities was reversed. Since the differences seem to be considerably larger than experimental error, it follows that no one-parameter interpretation of the changes in the alkylbenzene 2600A bands can be extended even approximately to the shorter wave-length bands. The need for more than one parameter in the 2600A bands has been remarked on by various authors.<sup>3,5</sup>

<sup>5</sup> Theodore Förster, *Zeits. f. Naturforschung* **2a**, 149 (1947).

In the meta sequence from benzene to mesitylene in Fig. 1, the red shifts with alkyl substitution are seen to be quite regular, about 1200–1500  $\text{cm}^{-1}$  for each additional methyl group. These are several times as large as the shifts in the 2600A bands. The  $f$  value for mesitylene is low as it is for *p*-xylene, almost as low as for benzene itself. Symmetrical substitution with permanent dipole moment zero, seems to lead to low oscillator strength in these bands. In the 2600A bands, mesitylene has lower intensity than *m*-xylene, but *p*-xylene has higher.<sup>4</sup>

The spectra of N-trimethyl and B-trimethyl borazole have been obtained in this laboratory and will be compared in a subsequent paper with the spectrum of mesitylene, which they resemble.

We are indebted to Mr. Charles Rector for his able assistance in taking and in reducing the plates.

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### Erratum: Heats of Dissociation of the $\text{N}_2$ Molecule and the $\text{NH}$ Radical

[*J. Chem. Phys.* **16**, 602 (1948)]

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The Figs. 1 and 2 should be interchanged leaving the legend as printed.