592. *The Infrared Vibrations of a s-Butyl Group attached to an Aromatic Ring.*

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s-Butyl groups attached to an aromatic ring show weak bands at 957 ± 2, 995 ± 3, and 1016 ± 1 cm.$^{-1}$ which appear to be characteristic. These correlations are useful in studies of aromatic rearrangements involving butyl groups.

THE strong out-of-plane C–H deformation modes (650—1000 cm.$^{-1}$) and the relatively weak in-plane deformation modes (950—1225 cm.$^{-1}$) of benzene derivatives are well known.[1,2] The methyl rocking frequencies also occur within this latter range, as described by Sheppard and Simpson.[3] Randle and Whiffen [4] reported that an isolated aromatic

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[1] Bellamy, "The Infrared Spectra of Complex Molecules," Methuen, London, 1958.

[2] Randle and Whiffen, Paper No. 12, Conference on Molecular Spectroscopy, 1954, Institute of Petroleum, p. 111.

[3] Sheppard and Simpson, *Quart. Rev.*, 1953, **7**, 19.

[4] Randle and Whiffen, *J.*, 1955, 3497.

methyl group gave rise to a characteristic absorption at *ca.* 1040 cm.$^{-1}$, while in *ortho*-dimethyl compounds, two bands appeared at *ca.* 995 and 1022 cm.$^{-1}$.

This paper records some observations made on a series of compounds containing s-butyl groups where it was noticed that weak absorptions occurred in the region 950—1020 cm.$^{-1}$ when the s-butyl group was attached to an aromatic ring.

TABLE 1. *Monoalkylbenzenes. Frequencies in cm.*$^{-1}$ (ε_A). (Values of ε_A less than 5 not recorded.)

No.	Subst.	γ(CH)			γ(CH)		Ring vibration		β(CH)
1	Et	902(7)			964		1002		1029(19) 1028(20) [6]
2	Pr^n	907(9)							1030(15) 1029 [5]
3	Pr^i	904(7)	920				999		1027(16) 1029 [5]
4	Bu^n	903(9)	929		964				1029(23) 1031 [5]
5	Bu^s	905(8)		955(7)		994(9)	1002	1015(10)	1030(14) 1031 [5]
6	Bu^t	904(6)	923				1002		1031(26) 1032 [5]

Table 1 records the frequencies and apparent molecular extinction coefficients (ε_A), which are comparable amongst themselves although different from the true molecular extinction coefficients, for a series of monoalkylbenzenes (Nos. 1—6) over the range 900—1030 cm.$^{-1}$.

The band at 1030 cm.$^{-1}$ in s-butylbenzene was ascribed by Randle and Whiffen [5] to an in-plane C–H deformation, and the band at 1002 cm.$^{-1}$ is the ring vibration reported by them [2] at 1001 ± 4 cm.$^{-1}$ (v). They reported an out-of-plane C–H deformation at 908 ± 10 cm.$^{-1}$ (mw), which is the 905 cm.$^{-1}$ band of s-butylbenzene. Two more out-of-plane C–H deformations were reported by them at 962 ± 6 cm.$^{-1}$ (w) and 982 ± 6 cm.$^{-1}$ (vw), neither of which was detected by Katritzky and Lagowski.[6] The former is undoubtedly the 964 cm.$^{-1}$ band in Nos. 1 and 4. By comparison of ε_A values for Nos. 1 and 4 (*i.e.*, 2 and 3 respectively), the 955 cm.$^{-1}$ band of s-butylbenzene does not appear to arise from this type of vibration.

Table 2 records similar data for polysubstituted benzene derivatives over the range 910—1035 cm.$^{-1}$. Compounds having a methoxy-group exhibited a very strong band at 1020—1037 cm.$^{-1}$ due to the C–O stretching, reported by Katritzky and Coats [7] at 1034 ± 8 cm.$^{-1}$; further, compounds with an isolated methyl group exhibited a weak band at 1035 ± 5 cm.$^{-1}$ due to the methyl rocking mode; these bands have not been recorded in the Table.

In *ortho*-disubstituted benzene derivatives (Nos. 7—13) the out-of-plane C–H deformation occurring [2] at 934 ± 11 cm.$^{-1}$ (w) was shown by all except No. 7, and the in-plane mode occurred within the limits quoted. In Nos. 11 and 12 it was hidden by the very strong ν(C–O) absorption of the methoxy-group. Another out-of-plane (C–H) deformation reported [2] at 977 ± 9 cm.$^{-1}$ (w) was missing in No. 9. The bands at *ca.* 957 cm.$^{-1}$ or *ca.* 994 cm.$^{-1}$ in Nos. 12 and 13 may arise from this vibration.

The in-plane C–H deformation of *para*-disubstituted benzene derivatives (Nos. 14—21) occurred close to the value (1013 ± 5 cm.$^{-1}$) quoted by Katritzky and Simmons [8] for compounds with an alkyl group and an electron-donating group as substituents. The out-of-plane C–H deformation [2] at 961 ± 12 cm.$^{-1}$ (w) was missing in Nos. 14—16. This may be the origin of the bands at *ca.* 956 cm.$^{-1}$ in Nos. 20 and 21 but they are considerably stronger than those in Nos. 17 to 19.

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[5] Randle and Whiffen, *Trans. Faraday Soc.*, 1956, **52**, 9.
[6] Katritzky and Lagowski, *J.*, 1958, 4155.
[7] Katritzky and Coats, *J.*, 1959, 2062.
[8] Katritzky and Simmons, *J.*, 1959, 2051.

In 1,2,4-trisubstituted benzenes (Nos. 22—34) an out-of-plane C–H deformation, an in-plane C–H deformation, and a ring vibration were shown by all the compounds, in agreement with values quoted by Randle and Whiffen [2] at 929 ± 11 (w), 1033 ± 10 (m) and 1001 ± 4 cm.$^{-1}$ (w) respectively.

TABLE 2. *Polysubstituted benzenes. Frequencies in cm.*$^{-1}$ (ε_A). (ε_A values less than 5 not recorded.)

ortho-*Disubstituted*

No.	Subst.	γ(CH)		γ(CH)				β(CH)
7	Me$_2$			984(15) [9]				1020(20) [9]
8	OH,Me	923(8), 928(5)		980(10) [9]				1037(25) [9]
9	OH,Pr^i	932(10)						1032(>30)
10	OH,Bu^n	934(11)		965				1037(>30)
11	OMe,Bu^n	928(10)		964				*
12	OMe,Bu^s	926(8)	956(7)		994(10)		1015(20) †	*
13	OH,Bu^s	932(9)	957(6)		997(10)		1015(9)	1028(21)

para-*Disubstituted*

No.	Subst.					β(CH)	
14	Pr$^i_2$	918(8)				1020(>30)	
15	Me,Pr^i					1019(15) [8]	
16	OH,Bu^t					1012(17)	
17	OH,Et	948		965		1015(7)	
18	OMe,Bu^n	933		963		1011(12)	
19	OH,Bu^n	923		966		1013(11)	
20	OMe,Bu^s	927	957(7)		994(11)	1010(9)	1016(14) †
21	OH,Bu^s	929	956(8)		995(10)		1014(20)

1,2,4-*Trisubstituted*

No.	Subst.					Ring breathing		
22	OH,Me,Bu^s	935	957(8)		993(9)	1004(9)		1017(7)
23	OMe,Me,Bu^s		959(6)		992(12)	1003(6)		1015(13) †
24	OMe,Bu$^s_2$	929	957(9)		994(18)	1000		1017(18) †
25	OH,Bu$^s_2$	934	958(17)		996(20)	1005		1017(15)
26	Me$_3$					999 [4]		
27	OH,Bu^s,Me	926, 937	955(9)		993(10)	1003(5)		1015(6)
28	OMe,Bu^s,Me	924	959(6)		992(8)	1006		1016(12) †
29	OH,Pr^i,Et	922, 934		978(6)				
30	OMe,Pr^i,Et	921		976(5)		1000		
31	OH,Me$_2$	928(9)		981			1010(7)	
32	Pr^i,OH,Me	944(>30)				1004		
33	OMe,Pr^i,Et	921		978(5)				
34	OH,Pr^i,Et	922, 934		978(6)		1002		

1,2,3,5-*Tetrasubstituted*

No.	Subst.					
35	Bu^s,OH,Me,Bu^s	933(9)	958(15)		996(18)	1015(15)
36	Bu^s,OH,Bu$^s_2$		957(21)		998(27)	1017(20)
37	Bu^s,OH,Bu^s,Me	936	959(14)		996(19)	1016(13)

* Hidden by very strong ν(C–O) at 1029—1037 cm.$^{-1}$.

† Determined on side of very strong ν(C–O) at 1029–1037 cm.$^{-1}$.

No out-of-plane or in-plane C–H deformations between 880 and 1160 cm.$^{-1}$ were reported by these authors [2] for 1,2,3,5-tetrasubstituted benzene derivatives.

Discussion.—It was noticed that whenever an s-butyl group was attached to an aromatic ring, three weak bands were present at 957 ± 2, 995 ± 3, and 1016 ± 1 cm.$^{-1}$, which could not be assigned to any C–H deformations of the ring; further, these bands were not shown with other alkyl groups. The increase of ε_A values when more than one s-butyl group was attached to the ring supported the idea that these bands arose from vibrations of the s-butyl group.

Sheppard and Simpson [3] reported the carbon–carbon stretching vibration of a paraffinic ethyl group at 1010 cm.$^{-1}$. Since the $C_{(2)}$–$C_{(3)}$ stretching vibration in an s-butyl group

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[9] Katritzky and Jones, *J.*, 1959 3670.

would resemble that of a paraffinic ethyl group, this may be the origin of the band at 1016 ± 1 cm.$^{-1}$.

The same authors reported an absorption at 955 cm.$^{-1}$ for paraffinic isopropyl groups due either to a carbon–carbon stretching vibration or to a methyl rocking mode. Since in the compounds studied the s-butyl group was attached to a more rigid skeleton, the two bands at 957 ± 2 and 995 ± 3 cm.$^{-1}$ are, therefore, probably rocking modes of the α-methyl group.

These three absorptions, although weak and occurring in a highly complex region of the spectrum, have been found useful in studies of intermolecular and intramolecular aromatic rearrangements involving butyl groups.

Experimental.—The compounds examined were recrystallised or fractionally distilled before measurement and had m. p. or b. p. in agreement with literature values.

The spectra were determined on a Grubb-Parsons G.S. 2A, double-beam grating spectrometer in 0·24M-carbon disulphide solutions in a 0·91 mm. cell.

Apparent molecular extinction coefficients (ε_A) were calculated from $\varepsilon_A = (1/cl) \log_{10} (I_0/I)$, where c is concentration in moles per litre and l is the cell thickness in cm. No account has been taken of finite slit width, and relative values are considered not accurate to better than ±7%.

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