

Vibrational spectra of 1-Br-2,3 dimethylbenzene, 1-Br-2,4 dimethyl benzene, 1-Br-2,5 dimethylbenzene and 1-Br-2,6 dimethylbenzene

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The infrared absorption spectra of 1-Bromo-2,3 dimethyl benzene, 1-Bromo-2,4 dimethyl benzene, 1-Bromo-2,5 dimethyl benzene and 1-Bromo-2,6 dimethyl benzene have been recorded in the region 4000-250 cm^{-1} using Perkin-Elmer (Model 621) double beam grating spectrophotometer. The fundamental frequencies have been interpreted along with Wilson's notations. The combination frequencies, overtones and internal modes of vibrations of the substituents have also been analysed.

1. INTRODUCTION

The vibrational spectra of benzene and its derivatives have been extensively studied by a large number of workers (see the compilation by Varsanyi 1969). Most of the trisubstituted benzene derivatives studied so far (Green *et al* 1970) have either all light substituents (atomic mass less than 25) or all heavy* substituents (atomic mass more than 25). Only a few trisubstituted benzene derivatives have been studied in which there are mixed (heavy and light) substituents. (A) 1-Br-2,3 dimethyl benzene, (B) 1-Br-2,4 dimethyl benzene, (C) 1-Br-2,5 dimethyl benzene, and (D) 1-Br-2,6 dimethyl benzene (named hereafter as the compound A, B, C and D respectively) are mixed trisubstituted benzene derivatives. The spectra of these compounds have not been studied so far. We have recorded the infrared spectra of these compounds and report its tentative assignment in the present work. Raman and near ultraviolet spectra will be reported shortly.

2. EXPERIMENTAL

Compounds A, B and D were obtained from Koch-Light Laboratories Ltd., England, and the compound C was obtained from K & K Laboratories, New York, U.S.A. They were 99.99% pure and were used without further purification. The compounds are in the liquid state at room temperature. The infrared absorption spectra of these compounds in the liquid phase were recorded on Perkin-Elmer (Model 621) double beam spectrophotometer in the region 4000-250 cm^{-1} . The measurements of the bands are expected to be accurate within $\pm 5 \text{ cm}^{-1}$.

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3. RESULTS AND DISCUSSION

Assuming CH_3 to be a point mass, the compounds A, B and C belong to C_s symmetry. Their 30 fundamental vibrations, their intensities and assignments have been given in table 1. Their modes of vibrations in Wilson's notations have also been given in the table. Compound D belongs to C_{2v} symmetry (again taking CH_3 as mass point) and its fundamental vibrations, their intensities, their assignments and the modes of vibrations in Wilson's notations have been given in table 2.

Table 1. Fundamental Frequencies (cm^{-1}) of (A) 1-Br-2,3 dimethylbenzene, (B) 1-Br-2,4 dimethylbenzene and (C) 1-Br-2,5 dimethylbenzene

		1-Br-2,3 Dimethyl Benzene	1-Br-2,4 Dimethyl Benzene	1-Br-2,5 Dimethyl Benzene	Vibration Number	Assignments	
a'	ν_1	3075(4) [†]	3092(4)	3074(4)	2	$\nu(\text{C}-\text{H})$	
	ν_2	3030(5)	3040(5)	3048(5)	20a	$\nu(\text{C}-\text{H})$	
	ν_3	3022(5)	3022(5)	3032(6)	20b	$\nu(\text{C}-\text{H})$	
b	ν_4	1598(3)	1597(4)	1604(5)	8b	$\nu(\text{C}-\text{C})$	
	ν_5	1560(6)	1572(4)	1560(5)	8a	$\nu(\text{C}-\text{C})$	
	ν_6	1490(3)	1480(8)	1490(10)	19a	$\nu(\text{C}-\text{C})$	
	ν_7	1400(4)	1395(6)	1418(5)	19b	$\nu(\text{C}-\text{C})$	
	ν_8	1267(2)	1272(4)	1275(3)	14	$\nu(\text{C}-\text{C})$	
	ν_9	1222(2)	1233(4)	1210(3)	3	$\delta(\text{C}-\text{H})$	
	ν_{10}	1172(4)	1162(4)	1155(2)	15	$\delta(\text{C}-\text{H})$	
	ν_{11}	1115(2)	1118(3)	1112(2)	18b	$\delta(\text{C}-\text{H})$	
	ν_{12}	(1050)*	1054(3)	1065(2)	7a	$\nu(\text{C}-\text{X})$	
	ν_{13}	1018(4)	1025(10)	1038(10)	13	$\nu(\text{C}-\text{X})$	
c	ν_{14}	955(2)	940(2)	955(2)	1	$\nu(\text{C}-\text{C})$	
	ν_{15}	765(10)	722(4)	732(3)	7b	$\nu(\text{C}-\text{X})$	
	ν_{16}	630(2)	627(3)	647(3)	6a	$\delta(\text{C}-\text{C}-\text{C})$	
	ν_{17}	550(2)	536(2)	545(3)	12	$\delta(\text{C}-\text{C}-\text{C})$	
	ν_{18}	470(3)	480(4)	465(4)	6b	$\delta(\text{C}-\text{C}-\text{C})$	
	ν_{19}	368(4)	380(4)	380(4)	9b	$\delta(\text{C}-\text{X})$	
	ν_{20}	312(2)	332(2)	305(2)	18a	$\delta(\text{C}-\text{X})$	
	ν_{21}	230(2)	(220)	(220)	9a	$\delta(\text{C}-\text{X})$	
	a''	ν_{22}	990(4)	982(4)	978(4)	5	$\gamma(\text{C}-\text{H})$
		ν_{23}	852(2)	868(4)	865(4)	17b	$\gamma(\text{C}-\text{H})$
ν_{24}		828(5)	803(8)	802(9)	11	$\gamma(\text{C}-\text{H})$	
ν_{25}		698(6)	700(3)	688(3)	4	$\gamma(\text{C}-\text{C}-\text{C})$	
ν_{26}		572(2)	565(3)	564(3)	16a	$\gamma(\text{C}-\text{C}-\text{C})$	
ν_{27}		445(3)	433(4)	455(4)	16b	$\gamma(\text{C}-\text{C}-\text{C})$	
ν_{28}		352(3)	353(3)	355(3)	10a	$\gamma(\text{C}-\text{X})$	
ν_{29}		250(2)	(250)	(250)	10b	$\gamma(\text{C}-\text{X})$	
ν_{30}		(132)	(130)	(130)	17a	$\gamma(\text{C}-\text{X})$	

ν = stretching, δ = in-plane bending, γ = out-of-plane bending.

[†] The figure in the bracket against the wavenumber indicates the intensity in the scale of 1 to 10.

* The fundamental frequencies within the brackets are predicted values.

Table 2. Fundamental frequencies (cm^{-1}) of (D) 1-Br-2,6 dimethylbenzene

		1-Br-2,6 Dimethyl- Benzene	Vibration Number	Assignments
a_1	ν_1	3087(4)	2	$\nu(\text{C-H})$
	ν_2	3063(5)	20a	$\nu(\text{C-H})$
	ν_3	1590(4)	8b	$\nu(\text{C-C})$
	ν_4	1445(5)	19b	$\nu(\text{C-C})$
	ν_5	1265(2)	11	$\nu(\text{C-C})$
	ν_6	1083(2)	9a	$\delta(\text{C-H})$
	ν_7	1038(10)	1	$\nu(\text{C-C})$
	ν_8	764(10)	12	$\delta(\text{C-C-C})$
	ν_9	580(3)	6a	$\delta(\text{C-C-C})$
	ν_{10}	432(2)	18b	$\delta(\text{C-X})$
	ν_{11}	(260)	15	$\delta(\text{C-X})$
a_2	ν_{12}	885(2)	17a	$\gamma(\text{C-H})$
	ν_{13}	528(5)	16a	$\gamma(\text{C-C-C})$
	ν_{14}	(220)	10a	$\gamma(\text{C-X})$
b_1	ν_{15}	995(6)	4	$\gamma(\text{C-C-C})$
	ν_{16}	950(2)	17b	$\gamma(\text{C-H})$
	ν_{17}	785(2)	11	$\gamma(\text{C-H})$
	ν_{18}	480(5)	16b	$\gamma(\text{C-C-C})$
	ν_{19}	300(2)	10b	$\gamma(\text{C-X})$
	ν_{20}	(130)	5	$\gamma(\text{C-X})$
b_2	ν_{21}	3026(4)	20b	$\nu(\text{C-H})$
	ν_{22}	1578(3)	8a	$\nu(\text{C-C})$
	ν_{23}	1160(10)	19a	$\gamma(\text{C-C})$
	ν_{24}	1295(2)	3	$\delta(\text{C-H})$
	ν_{25}	1193(2)	9b	$\delta(\text{C-H})$
	ν_{26}	1162(3)	7a	$\nu(\text{C-X})$
	ν_{27}	1010(7)	13	$\nu(\text{C-X})$
	ν_{28}	535(4)	7b	$\nu(\text{C-X})$
	ν_{29}	440(4)	6b	$\delta(\text{C-C-C})$
	ν_{30}	(262)	18a	$\delta(\text{C-X})$

For the assignment of the fundamental vibrations of the compounds A, B and C belonging to C_s symmetry, we have taken help of the mixed trisubstituted benzene derivative 1-chloro-2-methyl-4-fluorobenzene whose i.r. spectrum has been interpreted by Green (1971). Correspondence to different vibration numbers in Wilson's notations are based on the work of Varsanyi (1969).

Similarly for the assignment of the fundamental vibrations of the compound D belonging to C_{2v} symmetry, we have taken help of the analysis of the i.r. spectrum of 1-chloro-2,6-dimethylbenzene interpreted by Green (1971).

1. Fundamental Vibrations

The fundamental vibrations can be classified into three main groups :

(a) *Stretching Vibrations (ν)* :

(i) *C-H stretching vibrations and C-X stretching vibrations* : These vibrations of trisubstituted benzenes are derived from the C-H stretching vibrations of benzene. Benzene has six modes of C-H stretching vibrations denoted by 20a, 20b, 2, 13, 7a and 7b. Two modes 20 and 7 are degenerate and have the frequencies 3080 (e_{1u}) and 3046 (e_{2g}) cm^{-1} while the other two modes 2 and 13 have the frequencies 3062 (a_{1g}) and 3060 (b_{1u}) cm^{-1} respectively. In the case of trisubstituted benzenes, out of these six modes, three modes remain as C-H stretching and three become C-X stretching, where X is the substitution for H atom in benzene. To be more precise X represents the first atom of the substituent which is in direct chemical bonding with one of the carbon atoms in the ring.

For mixed trisubstitution C-H stretching modes are 2, 20a and 20b, and the remaining three modes viz., 13, 7a and 7b belong to C-X stretching vibration. It is evident from the wavenumbers of these fundamentals for compounds A, B and C that the frequencies of C-H stretching modes lie between 3000 and 3100 cm^{-1} whereas the frequencies of C-X stretching modes decrease considerably. Corresponding to light substituents the stretching frequencies are above 1000 cm^{-1} , whereas for heavier substituent X = Br the stretching frequency drops below 800 cm^{-1} . For compound D and C-H stretching frequencies have been assigned at ν_1 (3087 cm^{-1}), ν_2 (3062 cm^{-1}) and ν_{21} (3026 cm^{-1}), whereas the C-X stretching vibrations are ν_{26} (1162 cm^{-1}), ν_{27} (1010 cm^{-1}) and ν_{28} (535 cm^{-1}). These assignments are in agreement with the frequencies calculated by normal coordinate analysis of the compounds of this nature by McMurry & Thornton (1952) and with those interpreted by Green *et al* (1971, 1972).

(ii) *C-C stretching vibrations and C-C ring breathing* : The vibration modes 8a, 8b, 19a, 19b, 14 and 1 of benzene having frequencies 1585 (e_{2g}), 1485 (e_{1u}), 1310 (b_{2u}) and 992 (a_{1g}) cm^{-1} are the C-C stretching vibrations. On substitution the frequencies of the first five modes remain almost unchanged, whereas the frequency of mode 1 is decreased in C_s symmetry and is increased in C_{2v} symmetry.

For compounds A, B and C these frequencies have been denoted by ν_4 , ν_5 , ν_6 , ν_7 , ν_8 and ν_{14} for modes 8b, 8a, 19a, 19b, 14 and 1 respectively. The frequencies assigned to these fundamentals agree well with the results of Green (1971, 1972) and others (Varsanyi 1969).

For compound D these frequencies are ν_3 (1590 cm^{-1}), ν_4 (1445 cm^{-1}), ν_5 (1265 cm^{-1}), ν_7 (1928 cm^{-1}), ν_{22} (1578 cm^{-1}) and ν_{23} (1460 cm^{-1}) for these modes. These assignments are in agreement with the earlier works.

(b) *In-Plane-Bending Vibrations (δ)*

(i) *C-H In-Plane Bending Vibrations and C-X In-Plane Bending Vibrations* : These in-plane bending vibrations for trisubstituted benzene are derived from the C-H in-plane bending vibrations of benzene. There are six modes in C-H

in-plane bending vibrations of benzene denoted in Wilson's notations by 3, 9a, 9b, 15, 18a and 18b having the magnitudes 1326 (a_{2g}), 1178 (e_{2g}), 1150 (b_{2u}) and 1033 (e_{1u}) cm^{-1} respectively.

In trisubstituted benzene derivatives three modes of vibration remain almost unaltered and are called (C-H) in-plane bending vibrations and three modes change considerably in frequency, assuming the character of C-X in-plane bending vibrations.

In asymmetric (C_s) trisubstitution modes 3, 15 and 18b remain as C-H in-plane bending and modes 9a, 9b and 18a become C-X in-plane bending vibrations. In table 1 the $\delta(\text{C-H})$ frequencies have been denoted by ν_9 , ν_{10} and ν_{11} , their magnitudes lying between 1233 and 1115 cm^{-1} , and the $\delta(\text{C-X})$ frequencies have been denoted by ν_{21} , ν_{19} and ν_{20} , their magnitudes have decreased considerably, lying below 400 cm^{-1} . These assignments are in agreement with Green (1971) and others.

In vicinal trisubstitution (e_{2v}), modes 3, 9a, and 9b are regarded as C-H in-plane bending vibrations while 15, 18a and 18b become C-X in-plane bending vibrations. For compound D the frequencies for C-H in-plane bending modes are 1295, 1083 and 1193 cm^{-1} and are denoted by fundamentals ν_{24} , ν_6 and ν_{25} respectively; whereas C-X in-plane bending vibrations are expected to be $\nu_{11} = 260$, $\nu_{30} = 262$ and $\nu_{10} = 432$ cm^{-1} for modes 15, 18a and 18b respectively (Table 2). These assignments are in accordance with Plyler (1948, 1950) and the frequency range given by Varsanyi (1969). According to Varsanyi, the frequency sequence is $\nu'_{18b} > \nu'_{18a} \approx \nu'_{15}$. For vicinal trisubstituted benzenes the C-X in-plane bending vibration for mode 18b is the highest among all the $\delta(\text{C-X})$ frequencies and it is nearly 400 cm^{-1} for trichlorobenzene. The frequency ranges of the other two vibrations are overlapping. On the basis of these facts the above assignments have been made. These are in good agreement with data of Green *et al* (1971, 1972) as well as other workers for similar compounds.

(ii) *C-C-C In-plane bending vibrations*: Normal modes 6a, 6b and 12 are regarded as the C-C-C in-plane bending vibrations. The benzene frequencies for these modes are 606 (e_{2g}) and 1010 (b_1) cm^{-1} respectively.

For mixed light (l) and heavy (h) substitutions for the forms 1- h -2, 3 l_2 , 1- h -2, 4 l_2 , 1- h -2, 5 l_2 and 1- h -2, 6 l_2 as we have considered the compounds A, B, C and D the frequency of mode 6a increases while that of 6b decreases with respect to benzene frequency (Varsanyi 1969).

In asymmetric trisubstitution the frequency interval of normal mode 6a lies between 600 and 750 cm^{-1} and that of 6b appears below 500 cm^{-1} . The frequencies assigned for C-C-C in-plane bending vibrations for compounds A, B and C for modes 6a and 6b are as follows:

Mode 6a (ν_{16}): 630, 627 and 647 cm^{-1}

Mode 6b (ν_{18}): 470, 480 and 465 cm^{-1} .

For compound D the frequencies for modes 6a and 6b have been assigned at 580 cm^{-1} (ν_9) and 440 cm^{-1} (ν_{29}) respectively. These assignments are in agreement with the values reported by Green (1971) for other mixed vicinal trisubstituted benzene derivatives.

Mode 12 in benzene has a frequency 1010 cm^{-1} but in asymmetric mixed trisubstituted benzenes the frequency is decreased considerably and drops to nearly 550 cm^{-1} whereas in vicinal mixed trisubstitution (C'_{2v}) the frequency is decreased to 764 cm^{-1} nearly. These frequencies have been denoted by ν_{17} in table 1 and ν_8 in table 2.

(c) *Out-of-Plane Bending Vibration (γ)*

(i) *C-H Out-of-plane bending vibrations and C-X out-of-plane bending vibrations*: There are six C-H out-of-plane vibrations in benzene corresponding to the modes 5, 17a, 17b, 10a, 10b and 11 whose frequencies are at 985 (b_{2g}), 970 (e_{2g}), 849 (e_{1g}) and 671 (e_{2u}) cm^{-1} respectively.

In trisubstituted benzene derivatives three modes remain as $\gamma(\text{C-H})$ and three modes become $\gamma(\text{C-X})$.

In asymmetric trisubstitution (C'_s) for mixed or heavy substituents the C-H out-of-plane vibrations are modes 5, 17b and 11 and the C-X out-of-plane modes are 10a, 10b and 17a. In table 1 these modes have been assigned as ν_{22} , ν_{23} , ν_{21} for $\gamma(\text{C-H})$ and ν_{28} , ν_{29} and ν_{30} for $\gamma(\text{C-X})$. $\gamma(\text{C-H})$ modes have frequencies near the corresponding benzene frequencies, whereas $\gamma(\text{C-X})$ frequencies become very low. In this case the highest frequency for $\gamma(\text{C-X})$ has been assigned near 350 cm^{-1} (ν_{28}) for mode 10a, whereas the frequencies for modes 10b and 17a are anticipated to be below 250 cm^{-1} . In the absence of Raman data these low frequencies can not be confirmed.

In case of vicinal trisubstituted benzene (C'_{2v}) for mixed or heavy substituents the C-H out-of-plane vibrations are represented by modes 17a, 17b and 11, whereas (C-X) out-of-plane vibrations are the remaining modes 5, 10a and 10b. The $\gamma(\text{C-H})$ frequencies have been assigned at 885 (ν_{12}), 690 (ν_{16}) and 785 (ν_{17}) cm^{-1} respectively, whereas $\gamma(\text{C-X})$ frequencies are very low, one frequency ν_{10} lies at 300 cm^{-1} and others are expected to lie below 250 cm^{-1} .

These assignments are in agreement with the frequency intervals established by Whiffen (1955) and McMurry & Thornton (1952) by normal coordinate analysis and experimental values reported by Varsanyi (1969).

(ii) *C-C-C Out in-plane bending vibrations*: Normal modes 4, 16a and 16b are the C-C-C out-of-plane bending vibrations of benzene, the corresponding frequencies being 703 (b_{2g}) and 405 (e_{2u}) cm^{-1} respectively.

In asymmetric mixed trisubstitution the frequency of mode 4 decreases slightly from its magnitude in benzene, whereas for symmetric and vicinal trisubstitution the frequency increases rapidly and may be as high as 998 cm^{-1} .

The frequencies assigned for mode 4 (ν_{25}) for asymmetric compounds A, B and C are at 698, 700 and 688 cm^{-1} respectively, whereas for compound D the frequency assigned for this mode (4) is at 995 cm^{-1} (ν_{15}).

The frequencies in trisubstituted benzenes for modes 16a and 16b increase from the corresponding benzene values (405 cm^{-1}). The frequency of 16a is always higher than that of 16b.

For asymmetric trisubstitution Bentley & Wolfarth (1959) assigned one component 16a between 530 and 590 cm^{-1} in the infrared spectrum of asymmetric trialkyl benzenes, while the other component 16b was assigned in the interval 430-440 cm^{-1} . Shimanouchi *et al* (1956) calculated the frequency for vibrational pair 16 by normal coordinate analysis and obtained the values 588 and 441 cm^{-1} respectively. The assignments for compounds A, B and C for mode 16a and 16b are in agreement with the above results. The fundamentals for these modes are ν_{26} and ν_{27} respectively in table 1.

Bogomolov (1962) calculated the frequencies for the modes 16a and 16b for vicinal trimethyl benzene and found the values at 482 and 478 cm^{-1} respectively. The frequency interval for vicinal trisubstitution has been established between 530 and 540 cm^{-1} for mode 16a and between 470-480 cm^{-1} for mode 16b (Varsanyi 1969).

The frequencies assigned for compound D for modes 16a and 16b and 528 (ν_{13}) and 480 (ν_{18}) cm^{-1} respectively which are in agreement with the interval established by several workers (Singh *et al* 1968 and Varsanyi 1969).

2. Combination and Overtone Frequencies

Combination and overtone bands have also been observed. These bands have been analysed below :

(A) 1-Br-2,3 Dimethylbenzene :

1138 : 312 + 828; 1392 : 1018 + 368; 1465 : 990 + 470;
 1545 : 990 + 550; 1518 : 828 + 698; 1508 : 955 + 572 or 2 \times 765;
 1655 : 1018 + 630 or 2 \times 828; 1855 : 1018 + 852 and 1920 : 2 \times 955.

(B) 1-Br-2,4 Dimethylbenzene :

1105 : 627 + 480; 1124 : 700 + 433; 1248 : 700 + 536;
 1375 : 803 + 565; 1562 : 868 + 700; 1622 : 1054 + 565;
 1667 : 940 + 722; 1718 : 1025 + 700; 1740 : 2 \times 868;
 1800 : 1025 + 803; 1883 : 2 \times 940; 1922 : 1395 + 536.

(C) 1-Br-2,5 Dimethylbenzene :

1012 : 564 + 455; 1355 : 732 + 647; 1392 : 2 \times 688;
 1460 : 2 \times 732; 1510 : 955 + 545; 1530 : 978 + 564;
 1830 : 955 + 865; 1892 : 2 \times 955.

(D) 1-Br-2,6 Dimethylbenzene :

1240 : 764 +480; 1378 : 220 +1162; 1400 : 885 + 535;
 1560 : 2 × 795; 1535 : 2 × 764, 1660 : 1193 +480;
 1727 : 1174 +580; 1855 : 1083 +795; 1918 : 2 × 960.

3. Internal Vibrations of the Substituent Groups

The absorptions arising from the methyl (CH₃) groups in the side chain of the benzene ring may be CH₃ stretching vibrations, CH₃ symmetric and anti-symmetric deformations, their overtones and CH₃ rocking vibrations. The frequencies of the observed bands for the internal vibrations of the CH₃ groups have been assigned according to Green (1970) and have been given in table 3 for the compounds A, B, C and D.

Table 3. CH₃ Frequencies (cm⁻¹) in Compounds A, B, C and D

Mode of Vibration	(A) 1-Br-2,3 Dimethyl Benzene	(B) 1-Br-2,4 Dimethyl Benzene	(C) 1-Br-2,5 Dimethyl Benzene	(D) 1-Br-2,6 Dimethyl Benzene
ν_{as} (CH ₃)	2980	2984	2980	2982
ν_{as} (CH ₃)	2950	2960	2957	2960
ν_s (CH ₃)	2930	2930	2930	2930
$2\delta_{as}$ (CH ₃)	2870	2870	2865	2860
$2\delta_s$ (CH ₃)	2743	2738	2740	2738
δ_{as} (CH ₃)	1452	...	1440	...
δ_{as} (CH ₃)	1438	1436
δ_s (CH ₃)	1383	1382	1383	1378
(CH ₃) rocking	...	1025	1038	1028
	1002	990	1000	1010

ν = stretching, δ = deformation, s = symmetric, as = antisymmetric.

It is evident that the internal modes of vibrations of the substituents are little affected due to the change in its positions in the benzene ring.

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