

THE INFRARED SPECTRA OF ORTHO META AND PARA THIOCREOLS

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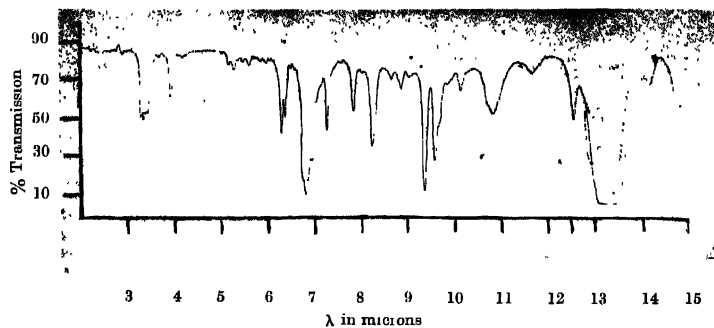
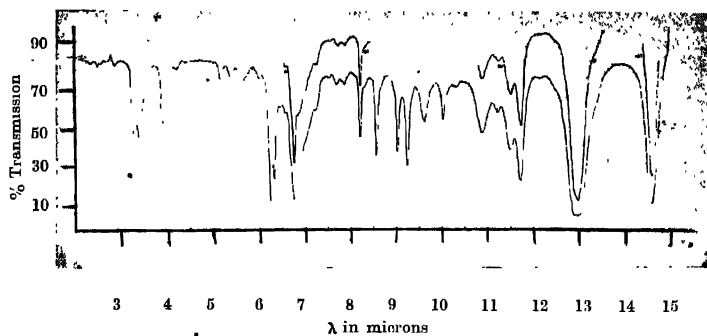
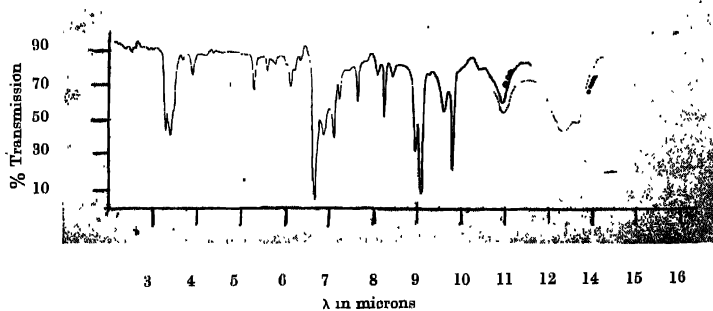
ABSTRACT. The infrared spectra of the *o*-, *m*-, and *p*- thiocresols were taken on the Perkin Elmer infrared spectrophotometer between the region 2 to 15 microns. The S-H stretching frequency is reported to be near about 2580 cm^{-1} . This characteristic frequency was observed to be present in all the three molecules the values being 2577, 2577 and 2571 cm^{-1} in ortho, meta and para thiocresols respectively. The frequencies arising out of phenyl and methyl parts have been assigned to their respective modes of vibration.

INTRODUCTION

The ultraviolet vapour absorption of these molecules was undertaken and to assign frequencies to definite modes of vibration, it was thought necessary to take the infrared spectra of these molecules as the data were not available. The samples were supplied by Eastman Kodak Company. The infrared spectra of toluene, thiophenol and cresols are known and a comparative study in a tabular form is carried out to bring out the broad features in the spectra of these molecules with the substitution of SH in thiocresols in place of OH in cresols.

EXPERIMENTAL

The infrared spectra of all the three molecules were recorded on the Perkin Elmer infrared spectrophotometer using sodium chloride optics. In case of para thiocresol the substance was dissolved in carbon tetrachloride and then introduced in between the plates of sodium chloride and the thickness was 0.1 mm and kept in the absorption path. The other pair of plates contained only carbon tetrachloride and was kept in the absorption path in front of the second aperture. The light source is divided in two beams and one passes through the solution and the other through the solvent. In the case of meta and ortho thiocresols the substances were introduced directly in between the plates having the film thickness of 0.025 mm and kept in front of one of the apertures. In front of the second aperture only one plate of sodium chloride having the same thickness as the total thickness of these two plates was kept. In case of broad bands, in order to define them further the strength of the solution was made less in case of para thiocresol while in case of meta and ortho thiocresols the film was made thin by introducing a drop between the plates and pressing them together. In figures 1, 2 and 3 the infrared spectra of the three molecules ortho, meta and para thiocresols respectively are given.

Fig. 1. Infrared absorption spectrum of *o*-thioresol.Fig. 2. Infrared absorption spectrum of *m*-thioresol.Fig. 3. Infrared absorption spectrum of *p*-thioresol.

RESULTS

All these three molecules show an absorption band near about 2580 cm^{-1} , and another absorption band between 1200 and 1210 cm^{-1} . All the bands observed in the case of the three molecules are given in Table I together with the infrared absorption bands for toluene, thiophenol, ortho, meta and para cresols for comparing them with the absorption bands in ortho, meta and para thiocresols with the intensities for the same.

DISCUSSION

Of the three cresols, *p*-thiocresol belongs to the C_{2v} symmetry and the other two to C_2 symmetry. Para-thiocresol has 15 A_1 , 3 A_2 , 14 B_1 , and 10 B_2 vibrations whereas ortho and meta thiocresols have 29 A' and 13 A'' vibrations. Except for the 3 A_2 vibrations in case of para thiocresol all others are active both in Raman and infrared. The assignment of these vibrations is proposed on the basis of comparison with thiophenol on one hand and toluene on the other. These are also compared with the corresponding cresols.

The phenyl vibrations :

Table II gives the correlation of the phenyl vibrations¹ (Herzfeld *et al*, 1946) with those of thio-cresols. The six C-C stretching vibrations including ring breathing vibration are assigned to the frequencies as indicated in table. The e_g vibration 1596 of benzene gives rise to two bands around 1600 corresponding to a_1 and b_1 in C_{2v} and a' in C_2 . It is important to observe that the corresponding bands are rather weak in para thiocresol. In paracresol there are two strong bands at 1600 and 1616 . In *p*-thiocresol there is only one strong maximum near 1631 with shoulders at 1575 and 1608 . The bands 1631 and 1608 are assigned to these two modes in *p*-thiocresol. Two bands are also expected corresponding to $1485\ e_u$ of benzene. This region is, however, complicated by the fact that there are also bands corresponding to symmetric and asymmetric C-CH₃ bending vibrations in this region. Two bands one near 1480 and other near 1400 are assigned to these. The breathing vibration $992\ a_{1g}$ of benzene drops to between 772 to 789 in thiocresols.

The C-H stretching region near 3000 cm^{-1} is not well resolved and only a tentative assignment is proposed. The C-H in plane and deformation vibration lying between 1280 and 1600 cm^{-1} have been assigned. It is observed that the spectrum of the meta compound usually gives rise to a number of strong bands in this region. From the correlation of other benzene derivatives the assignments given in the table are proposed. The out of plane deformation vibrations are assigned by comparison with other disubstituted benzenes.

TABLE I
 Infrared frequencies

Toluene cm ⁻¹ Int.	Thiophenol cm ⁻¹ Int.	<i>o</i> -Cresol cm ⁻¹ Int.	<i>o</i> -Thioresol cm ⁻¹ Int.	<i>m</i> -Cresol cm ⁻¹ Int.	<i>m</i> -Thioresol cm ⁻¹ Int.	<i>p</i> -Cresol cm ⁻¹ Int.	<i>p</i> -Thioresol cm ⁻¹ Int.
4651 (mrv)	4785 (w)	4545 (vw)	4545 (vw)	4386 (vw)	4545 (vw)	4367 (w)	4444 (vw)
4405 (sh)	4444 (vw)				4310 (vw)		4255 (vw)
4292 (mrv)	4098 (m)					4098 (w)	4098 (w)
4049 (m)	4032 (sh)			4016 (vw)	4032 (vw)		4000 (vw)
3861 (sh)	3788 (w)		3846 (vw)				
3676 (w)	3731 (w)						
3460 (w)	3484 (m)		3484 (vw)		3484 (vw)		3472 (vw)
3040 (s)	3086 (s)	3344 (ms)		3289 (m)		3322 (s)	
2924 (e)	2941 (m)	3049 (ms)	3067 (m)	3021 (m)	3087 (m)	3021 (m)	3030 (m)
2874 (e)	2899 (sh)	2933 (ms)	3021 (m)	2907 (m)	2941 (m)	2915 (m)	2924 (m)
2747 (m)	2747 (w)	2874 (m)	2941	2833 (m)		2874 (sh)	
			2747 (vw)	2782 (m)	2747 (vw)	2725 (w)	2725 (vw)
2597 (mrv)	2584 (e)	2590 (w)	2577 (m)	2681 (m)		2688 (w)	
		2518 (w)		2564 (m)	2577 (m)	2611 (w)	2571 (w)
2551 (sh)							

TABLE I (cont'd.)

Toluene cm ⁻¹ Int.	Thiophenol cm ⁻¹ Int.	o-Cresol cm ⁻¹ Int.	o-Thiocresol cm ⁻¹ Int.	m-Cresol cm ⁻¹ Int.	m-Thiocresol cm ⁻¹ Int.	p-Cresol cm ⁻¹ Int.	p-Thiocresol cm ⁻¹ Int.
2415 (w)	2451 (sh)	2444 (w)	2415 (vw)	2475 (w)	2410 (vw)	2475 (w)	2475 (w)
2364 (sh)				2439 (w)	2381 (vw)	2347 (w)	2299 (vw)
2336 (w)	2358 (ms)						
2315 (sh)	2294 (w)						
2257 (w)	2273 (w)			2208 (w)			
2203 (w)	2232 (w)						
2165 (w)	2183 (w)	2092 (w)		2088 (w)		2079 (w)	
2110 (w)	2105 (w)	2053 (vw)		2016 (w)		1988 (w)	
2070 (w)	2058 (w)	1996 (w)	2000 (vw)	1949 (vw)			
1984 (sh)	1953 (s)	1934 (m)	1949 (vw)	1919 (vw)	1942 (w)		
1946 (s)			1908 (w)	1890 (w)		1869 (mw)	1890 (m)
1859 (s)	1866 (s)	1883 (m)	1838 (vw)	1842 (w)	1862 (w)		
1802 (s)	1799 (s)		1795 (vw)	1812 (w)			
1776 (sh)		1769 (m)	1761 (vw)		1770 (w)	1757 (w)	1786 (w)
1736 (m)	1736 (s)		1745 (vw)	1733 (w)	1748 (sh)		
			1730 (vw)		1730 (sh)		1730 (vw)
			1712 (vw)				
1675 (w)	1706 (sh)	1690 (m)	1695 (vw)	1698 (w)	1712 (vw)		
			1684 (vw)		1698 (sh)		

TABLE I (contd.).

Toluene cm ⁻¹ Int.	Thiophenol cm ⁻¹ Int.	o-Cresol cm ⁻¹ Int.	o-Thiocresol cm ⁻¹ Int.	m-Cresol cm ⁻¹ Int.	m-Thiocresol cm ⁻¹ Int.	p-Cresol cm ⁻¹ Int.	p-Thiocresol cm ⁻¹ Int.
1653 (sh)	1695 (sh)		1658 (vw)		1664 (w)		1655 (sh)
			1645 (vw)				
1603 (s)	1639 (sh)		1595 (m)	1616 (s)	1603 (s)	1616 (s)	1631 (m)
1575 (m)	1582 (s)	1592	1577 (m) 1548 (vw)	1585 (s)	1582 (s) 1550 (w)	1600 (s)	1608 (vw)
1524 (m)	1522 (sh)		1527 (sh)		1522 (sh)		1575 (vw)
1495 (s)	1479 (s)	1490	1484 (sh)	1488 (s)	1479 (s)	1511 (s)	1497 (s)
			1475 (e)				
1462 (e)		1461	1462 (s)		1462 (sh)	1456 (s)	1451 (ms)
	1445 (s)		1443 (s)	1433 (ms)	1453 (sh)	1435 (s)	1403 (ms)
			1408 (sh)		1429 (sh)		
1377 (ms)	1383 (s)	1375	1381 (m)	1399 (m)	1401 (sh)	1380 (sh)	1379 (m)
	1370 (sh)			1364 (m)	1383 (w)		
1333 (sh)			1328 (vw)	1344 (ms)	1330 (vw)	1335 (sh)	1343 (w)
	1330 (s)	1344	1328 (ms)			1351 (s)	1305 (m)
1315 (m)	1303 (s)	1321	1303 (ms)	1324 (ms)	1302 (w)		
				1304 (m)			
1282 (sh)	1276 (m)	1295	1280 (m)	1279 (s)	1282 (vw)	1292 (m)	1271 (sh)
				1266 (s)			
1247 (m)	1236 (m)	1256	1250 (vw)	1233 (s)	1272 (vw)	1286 (s)	1252 (w)
1209 (ms)	1202 (sh)	1219	1217 (ms)			1214 (s)	1211 (m)
			1209 (sh)				
1178 (s)	1165 (s)	1207	1209 (ms)		1205 (sh)	1172 (s)	1182 (w)

TABLE I (contd.)

Toluene cm ⁻¹ Int.	Thiophenol cm ⁻¹ Int.	<i>o</i> -Cresol cm ⁻¹ Int.	<i>o</i> -Thiocresol cm ⁻¹ Int.	<i>m</i> -Cresol cm ⁻¹ Int.	<i>m</i> -Thiocresol cm ⁻¹ Int.	<i>p</i> -Cresol cm ⁻¹ Int.	<i>p</i> -Thiocresol cm ⁻¹ Int.
1187 (s)	1159 (ms)	1169 (ms)	1159 (w)	1156 (ms)	1168 (ms)		
			1139 (sh)				
1107 (s)	1120 (s)	1106 (ms)	1131 (w)		1109 (ms)	1117 (m)	1115 (ms)
			1111 (vw)				
1081 (s)	1094 (s)		1070 (s)	1088 (m)	1083 (ms)	1106 (s)	1099 (s)
1043 (sh)	1072 (s)	1043 (ms)	1046 (s)	1042 (m)	1041 (m)	1044 (mw)	1041 (m)
1031 (s)	1027 (s)		1035 (ms)				
1001 (sh)	1003 (s)		1016 (vw)	1011 (m)		1016 (mw)	1019 (s)
980 (w)	981 (m)	987 (ms)	988 (w)	1001 (m)	982 (m)	987 (w)	1002 (vw)
967 (sh)	960 (m)		966 (w)	966 (w)	971 (w)	952 (w)	956 (sh)
930 (w)	930 (w)	933 (m)	924 (m)	928 (ms)	919 (m)	927 (w)	913 (m)
896 (s)	898 (s)				891 (w)		
873 (w)	872 (sh)	844 (m)	856 (w)	892 (m)	870 (m)		
843 (m)	833 (ms)	818 (m)		852 (m)	853 (s)	842 (ms)	
					824 (vw)	816 (s)	827 (m)
785 (m)	796 (sh)		797 (m)	776 (s)	803 (sh)	805 (sh)	810 (m)
	786 (sh)		772 (s)	769 (s)	772 (vs)		789 (m)
728 (s)	735 (s)	751 (ms)	744 (s)	735 (m)		740 (ms)	751 (sh)
693 (s)	689 (s)	710 (ms)	705 (w)			703 (w)	725 (w)
	689 (s)			689 (m)	686 (s)		
	668 (s)		676 (w)				

N.B.—The infrared frequencies for toluene, thiophenol, *o*-cresol, *m*-cresol and *p*-cresol are taken from the A.P.I. Catalogue giving the infrared data.

TABLE II
Vibrations from benzene ring

	Benzene D_{6h}	<i>p</i> -thiocresol C_{2v}	<i>o</i> -thiocresol C_s	<i>m</i> -thiocresol C_s
C-C stretching }	a_{1g} 992	789 a_1	772 a'	772 a'
	b_{2u} 1310	1232 b_1	1250 a'	1272 a'
	e_{1u} 1485	1497 a_1	1475 a'	1479 a'
	e_{1u} 1485	1403 b_1	1408 a'	1401 a'
	e_{2g} 1596	1631 a_1	1595 a'	1603 a'
	e_{2g} 1596	1608 b_1	1577 a'	1582 a'
C-H stretching }	e_{2g} 3047	Raman 3136 b_1	— a'	Raman 3117 a'
	b_{1u} 3060	Raman 3061 a_1	— a'	Raman 3055 a'
	e_{1u} 3080	— a_1	3067 a'	3067 a'
	a_{1g} 3062	3030 a_1	3021 a'	Raman 3176 a'
C-H inplane deformation }	e_{2g} 1178	1182 a_1	1159 a'	1168 a'
	e_{1u} 1033	1019 a_1	1035 a'	1019 a'
	b_{2u} 1110	1115 b_1	1111 a'	1109 a'
	a_{2g} 1326	1271 b_1	1280 a'	1282 a'
C-H out of plane deformation }	e_{1g} 850	810 b_2	797 a''	803 a''
	e_{2u} 970	956 a_2	988 a''	982 a''
	e_{2u} 970	827 b_2	856 a''	853 a''
	b_{2g} 985	913 b_2	924 a''	919 a''
C-C inplane bending }	b_{1u} 1010	1099 a_1	1070 a'	1083 a'
	e_{2g} 606	639 a_1	661 a'	685 a'
	e_{2g} 606	— b_1	552 a'	523 a'
C-C out of plane bending }	b_{2g} 703	(—) b_2	676 a''	676 a''
	e_{2u} 404	(—) a_2	432 a''	410 a''
	e_{2u} 404	(—) b_2	146 a''	147 a''
C-X stretching }	e_{1u} 3080	(—) b_1	686 a'	686 a'
	e_{2g} 3047	1211 a_1	1217 a'	1218 a'

TABLE II (contd.)

	Benzene D _{6h}	<i>p</i> -thiocresol C _{2v}	<i>o</i> -thiocresol C _s	<i>m</i> -thiocresol C _s
C-X inplane bonding	<i>e</i> _{1u} 1033	(-) <i>b</i> ₁	(-) <i>a</i> '	(-) <i>a</i> '
	<i>e</i> _{2g} 1178	(-) <i>b</i> ₁	(-) <i>a</i> '	(-) <i>a</i> '
C-X out of plane bending	<i>a</i> _{2u} 671	(-) <i>b</i> ₂	(-) <i>a</i> "	(-) <i>a</i> "
	<i>e</i> _{1g} 850	(-) <i>a</i> ₂	(-) <i>a</i> "	(-) <i>a</i> "

TABLE III

Methyl vibrations in the three cresols, toluene and the three thio cresols

	Toluene	Cresols			Thiocresols		
		<i>o</i> -	<i>m</i> -	<i>p</i> -	<i>o</i> -	<i>m</i> -	<i>p</i> -
Asymmetric Stretching	2920	2933	2907	2915	2941	2941	2924
Symmetric Stretching	2870	2874	2833	2874	Expected (2870)	Raman (2870)	Expected (2870)
Symmetric bonding	1377	1375 or 1364	1399 1364	1380	1381	1383	1379
Asymmetric bonding	1460	1461	1488	1456	1462	1462	1451
	1436	1440 Raman	1433	1435	1443	1429	1403?
Rocking	1081	—	—	—	—	—	—
	1041	1043	1042	1044	1046	1041	1041

The inplane ring vibrations corresponding to *e*_g+ 606 of benzene give rise to two bands usually one above 606 cm⁻¹ and other below this value. The assignments of 552 and 553 cm⁻¹ in case of ortho and meta-thiocresols of one of the components is given by the Raman data. Out of plane ring vibrations corresponding to 703 *b*_{2g} of benzene is assigned to a weak band at 676 cm⁻¹ in ortho and meta thiocresols. The others are discussed in Raman effect. The substituent sensitive vibrations from the phenyl part are tabulated. In this stretching vibration one should correspond to C-CH₃ stretching (Pitzer and Scott, 1943) which is usually found near 1210 cm⁻¹ and the other C-S stretching. The latter vibration is known to occur near 680 cm⁻¹ as in other mercaptans (Sheppard, 1950). No definite assignment can however be made. The position of these and the corresponding C-S in-plane and out of plane bending is not satisfactory.

Methyl group gives rise to three C-H stretching and three C-H bending and two rocking vibrations. The general trend in these vibrations has been shown by various workers (Sheppard, 1953). The assignment of CH_3 modes is shown in table III.

The S-H stretching frequency is observed to be present at 2577, 2577 and 2571 cm^{-1} in ortho, meta and parathiocresols respectively.

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REFERENCES

- Horzfeld, N., Ingold, C. K. and Poole, H. G., 1946, *Jour. Chem. Soc.*, **316**,
Pitzer, K. S. and Scott, D. W., 1943, *Jour. Amer. Chem. Soc.*, **65**, 803
Sheppard, N., 1950, *Trans. Farad. Soc.*, **46**, 429.
Sheppard, N., 1953, *Quart. Revs.*, **7**, 19.
Trotter, I. F. and Thompson, H. W., 1946, *Jour. Chem. Soc.*, **481**.