

Vibrational Analyses of 2,4-Dichloropentane and 2,4,6-Trichloroheptane

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This study of the vibrational spectra of 2,4-dichloropentane and 2,4,6-trichloroheptane uses normal coordinate calculations as a probe for the presence of different molecular conformers. The calculations use a complete valence force field for secondary chlorides which was developed by fitting the observed vibrational frequencies of model compounds. Observed and calculated frequencies agree well. The results of these calculations on *dl* and meso 2,4-dichloropentane and on isotactic 2,4,6-trichloroheptane indicate the presence of conformers other than those which are accepted as sterically preferred.

INTRODUCTION

In order to elucidate the effect of stereochemical structure on conformation in poly-(vinyl chloride) (PVC), the dimer and trimer models of PVC have been studied extensively (1-6). In these investigations nuclear magnetic resonance (NMR), infrared and Raman spectroscopy have been the most effective tools. In NMR, chemical shifts and coupling constants are found to be directly related to molecular configuration. However, the interpretation of NMR spectra is not based on a simple superposition of chemical shifts and coupling constants but on a weighted average of these parameters. This complicated averaging, which is a function of the total conformational population of the compound being studied, renders NMR spectroscopy less satisfactory for identifying rotational isomers of molecules which exist as a mixture of more than two conformers. Because infrared and Raman spectra comprise a simple superposition of contributions from all isomeric structures in equilibrium, complete conformer analysis by normal coordinate calculations is theoretically possible (although spectral overlap between various structures often renders the interpretation of the vibrational spectra difficult). In previous studies (7, 8) we have developed a complete general valence force field for secondary chlorides. We present here the results of applying this force field to the analysis of the spectra of 2,4-dichloropentane and 2,4,6-trichloroheptane.

In this investigation of secondary chlorides we use a staggered molecular model, that is, one in which the dihedral angle associated with a given C-C-C-C unit can only assume the discrete values of -60° , $+60^\circ$ or $+180^\circ$. (Departures from these specific values may, of course, occur in the stable conformations of the actual molecules.) Within the framework of this approximation small molecules can exist in a limited number of geometrically unique conformations, e.g., one conformation for 2-chloro-

propane and three conformations for 2-chlorobutane. In such instances the interpretation of the vibrational spectra can be done almost uniquely by means of normal coordinate analyses. However, for each of the stereochemical isomers of 2,4-dichloropentane, six geometrically unique structures can be defined within the constraints of the staggered molecular model. Because of the overlap of the predicted absorption bands of these conformers, normal coordinate analyses alone cannot be used to determine the equilibrium conformer population of *dl*- and meso-2,4-dichloropentane. Until recently many of the staggered conformational structures of 2,4-dichloropentane, and similar molecules in which large constituents such as chlorine atoms and methyl groups approach one another closely, have been considered to be sterically forbidden. This constraint, in conjunction with NMR and infrared investigations, led to the conclusion that at room temperature only two of the six possible conformers of *dl*-2,4-dichloropentane were present, the *TT* (or ${}_H S_{HH} S_H$) and the *GG* (or ${}_H S_{CC} S_H$) forms. In meso-2,4-dichloropentane only the *TG'* (${}_H S_{HC} S_H$) conformation was believed to be present, in mobile equilibrium with its mirror image, *G'T* (${}_H S_{CH} S_H$). The dominant features of the infrared, Raman and NMR spectra of 2,4-dichloropentane are well explained by these major conformers. However, weak infrared bands in the highly diagnostic region of the carbon-chlorine stretching vibrations (9), relatively strong and characteristic far infrared bands (7), and the temperature behavior of NMR spectra (4) cannot be adequately interpreted in terms of this restricted conformer population.

The results of normal coordinate calculations on the rotational isomers of 2,4-dichloropentane and 2,4,6-trichloroheptane are reported here. The complete general valence force field used in these calculations predicts well the dominant vibrational frequencies of 2-chloropropane, 2-chlorobutane, 3-chloropentane, and 2,4-dichloropentane (8), as well as the spectrum of PVC and its deuterated derivatives (10). As we will see in the present paper, similar good agreement is obtained for 2,4,6-trichloroheptane. The apparent general success of this potential field, in conjunction with its inability to explain numerous less dominant spectral features in terms of preferred conformers, strongly suggests that other rotational isomers are present.

2,4-DICHLOROPENTANE

Successful interpretation of the infrared spectra of secondary chlorides depends to a large extent on our ability to analyze the region of the C-Cl stretching vibrations. The frequency of this normal mode is sensitive to the geometric arrangement of the substituents attached to the carbon atoms which are joined to the carbon-chlorine bond. It is often possible to predict the presence of certain rotational isomers by comparing the observed C-Cl stretching frequencies with the empirically determined value of this frequency as a function of the environment of the carbon-chlorine bond (3). This approach was used to analyze the spectrum of 2,4-dichloropentane.

dl-2,4-Dichloropentane

In the spectrum of *dl*-2,4-dichloropentane there are two strong absorptions at 606 and 627 cm^{-1} which are the two ${}_H S_H$ C-Cl stretching vibrations in the preferred ${}_H S_{HH} S_H$ (*TT*) conformation (see Table I). In addition, there is a weak band at 715 cm^{-1} which grows progressively weaker on cooling and is not present in the spectra of crystalline

Table I. Calculated Wave Numbers (in cm^{-1}) and Potential Energy Distributions of Conformers of d, l-2,4-Dichloropentane

Observed Wave Number ^a	Calculated Wave Number	Potential Energy Distribution ^b
	1. $\text{H}^{\text{S}}\text{H} \text{H}^{\text{S}}\text{H}$ (TT) Conformer	
	42 A ^c	$\tau_{\text{A}2}$ (96)
	58 B	$\tau_{\text{B}2}$ (90)
120	120 A	CCC(52), $w_{\text{A}1}$ (29)
150		$\text{H}^{\text{S}}\text{H} \text{C}^{\text{S}}\text{H}$ ^d
	240 A	$\tau_{\text{A}1}$ (96)
245vw	241 B	$\tau_{\text{B}1}$ (91)
273	267 A	$w_{\text{A}1}$ (43), $x_{\pi\text{A}}$ (39)
310	312 B	$x_{\pi\text{B}}$ (44), $w_{\text{B}1}$ (33)
343m	342 B	$x_{\pi\text{B}}$ (42), $w_{\text{B}1}$ (39)
368m	371 A	$w_{\text{A}2}$ (65), $w_{\text{A}1}$ (10)
460m	458 B	$w_{\text{B}2}$ (74), $w_{\text{B}1}$ (12)
476vw	472 A	$x_{\pi\text{A}}$ (28), CCC(26)
606s	603 B	x_{B} (84)
627s	625 A	x_{A} (81)
650w		$\text{H}^{\text{S}}\text{H} \text{H}^{\text{S}}\text{H}$ ^d
682w		$\text{H}^{\text{S}}\text{H} \text{C}^{\text{S}}\text{H}$ ^d
706w		$\text{H}^{\text{S}}\text{C} \text{H}^{\text{S}}\text{H}$ ^d
715w		$\text{H}^{\text{S}}\text{C} \text{C}^{\text{S}}\text{H}$ ^a
877ms	872 B	r(59), $\text{B}_{\text{B}1}$ (23)
	884 A	$\text{R}_{\text{A}2}$ (40), $\text{B}_{\text{A}1}$ (29)
938s	939 B	$\text{R}_{\text{B}1}$ (25), $\text{R}_{\text{B}2}$ (23)
978m	985 A	$\text{B}_{\text{A}2}$ (35), $\text{B}_{\text{A}1}$ (33)
1012s	1023 B	$\text{B}_{\text{B}2}$ (61), $\text{R}_{\text{B}1}$ (10)
1067m	1068 B	$\text{R}_{\text{B}1}$ (44), $\text{B}_{\text{B}1}$ (30)
1100vw	1102 A	$\text{R}_{\text{A}1}$ (54), t(10)
1125s	1119 A	$\text{R}_{\text{A}2}$ (21), $\text{B}_{\text{A}2}$ (19)
1132s	1139 B	$\text{R}_{\text{B}2}$ (42), $\text{H}_{\pi\text{B}}$ (10)
1191m	1188 A	t(28), $\text{H}_{\sigma\text{A}}$ (23)
1222vvw	2x606 = 1212	
1257s	1252 B	$\text{H}_{\sigma\text{B}}$ (85)
	1280 D	w(44), $\text{H}_{\pi\text{B}}$ (36)
1288s		
	1292 A	$\text{H}_{\sigma\text{A}}$ (51), t(25)
1325mw	1325 A	$\text{H}_{\pi\text{A}}$ (56), $\text{H}_{\text{A}1}$ (15)
	1361 B	U_{B} (48), w(23)
1379s	1381 A	U_{A} (89)

samples. This absorption at 715 cm^{-1} is evidence of the presence of the $\text{H}^{\text{S}}\text{C}^{\text{S}}\text{H}$ or GG conformation. The two $\text{H}^{\text{S}}\text{C}$ C-Cl stretching frequencies of this conformer are calculated at 627 and 714 cm^{-1} . The lower frequency mode is not observed since it is undoubtedly overlapped by the strong absorption at 627 cm^{-1} of the $\text{H}^{\text{S}}\text{H}^{\text{S}}\text{H}$ form.

Table I--(Continued)

Observed Wave Number ^a	Calculated Wave Number	Potential Energy Distribution ^b
1415ms	1397 B	$U_B(46), H_{TB}(19)$
	1427 A	$\delta(95)$
	1459 A	$A_{A1}(72), A_{A2}(18)$
1443s	1459 B	$A_{B1}(78), A_{B2}(20)$
1450m	1459 B	$A_{B2}(80), A_{B1}(10)$
	1460 A	$A_{A2}(72), A_{A1}(18)$

Calculated Wave Number	Potential Energy Distribution	Calculated Wave Number	Potential Energy Distribution ^b
2. $H^S H^S H^S H^S$ (TG') Conformer			
41	$\tau_{A2}(95)$	1012	$P_{B1}(32), B_{B2}(18)$
45	$\tau_{A2}(83)$	1042	$P_{A2}(32), R_{A1}(26)$
136	$CCC(53), W_{B2}(16), W_{B1}(11)$	1090	$R_{A1}(32), R_{A2}(14)$
228	$X_{TB}(44), W_{B1}(17), \tau_{A1}(14)$	1119	$R_{B1}(33), P_{A1}(11)$
241	$\tau_{B1}(97)$	1149	$E_{B2}(17), R_{B2}(16)$
245	$\tau_{A1}(80)$	1191	$t(42), H_y(31)$
311	$W_{A1}(58), X_{TA}(23)$	1249	$H_{\sigma A}(80)$
338	$W_{B1}(46), X_{TB}(34)$	1276	$H_{\tau A}(22), H_{\sigma B}(19)$
377	$X_{TA}(44), W_{A1}(20), W_{A2}(16)$	1302	$H_{\sigma H}(27), w(21)$
418	$W_{A2}(50), W_{B2}(21)$	1327	$H_{\tau B}(63), R_{B1}(18)$
553	$X_A(32), CCC(15), W_{B1}(11)$	1362	$v_A(31), w(30)$
615	$X_B(50), X_A(48)$	1383	$v_B(67), v_A(21)$
642	$X_B(46), X_A(22)$	1389	$v_A(43), v_B(16)$
862	$R_{A2}(36), R_{A1}(15)$	1432	$\delta(92)$
889	$r(44), R_{A2}(15)$	1459	$A_{A1}(70), A_{A2}(13)$
918	$R_{B1}(18), R_{B2}(18)$	1460	$A_{B1}(57), A_{B2}(27)$
998	$L_{A1}(42), E_{B2}(17)$	1460	$A_{A2}(70), A_{A1}(14)$
		1460	$A_{B2}(57), A_{B1}(26)$

3. $H^S CH^S H^S H^S$ (GG') Conformer			
47	$\tau_{B2}(72), \tau_{A2}(22)$	1011	$P_{B2}(31), P_{A1}(16)$
52	$\tau_{A2}(66), \tau_{B2}(24)$	1041	$E_{A2}(25), R_{B1}(22)$
131	$CCC(54), W_{B2}(18)$	1084	$R_{A2}(16), R_{A2}(14)$
237	$\tau_{A1}(65), X_{TA}(19)$	1127	$R_{A1}(33), r(10)$

At 682 cm^{-1} an infrared band is observed which is also present in the spectrum of the crystalline phase of *dl*-2,4-dichloropentane. From the results of normal coordinate calculations (Table I and Fig. 1), this band can only be explained by the presence of either the $H^S H^S H^S H^S$ (TG) or the $H^S H^S H^S H^S$ (GG') conformations. The Raman spectrum of *dl*-2,4-dichloropentane provides specific evidence that the 682 cm^{-1} band should be

Table I--(continued)

Calculated Wave Number	Potential Energy Distribution	Calculated Wave Number	Potential Energy Distribution
241	τ_{B1} (97)	1152	R_{B2} (28), R_{B1} (14)
252	τ_{A1} (29), W_{B1} (29)	1206	t (33), $H_{\sigma A}$ (23)
311	W_{B1} (50), $X_{\pi A}$ (24)	1246	$H_{\sigma B}$ (60), $H_{\sigma A}$ (28)
338	$X_{\pi B}$ (72), W_{A1} (14)	1261	$H_{\sigma A}$ (33), $H_{\sigma B}$ (26)
350	W_{A1} (39), W_{A2} (17)	1296	$H_{\pi A}$ (31), w (25)
420	W_{B2} (41), W_{A2} (22)	1345	$H_{\pi B}$ (49), t (20)
505	X_B (41), W_{A2} (24)	1363	U_A (42), w (29)
624	X_A (93)	1381	U_B (81)
701	X_B (52), ccc (19)	1393	U_A (43), w (16)
867	R_{A1} (32), R_{A2} (26)	1433	δ (87)
895	B_{A1} (32), r (27)	1459	A_{A1} (72)
899	R_{B1} (23), R_{B2} (21)	1460	A_{B1} (54), A_{B2} (23)
979	B_{B1} (51), $H_{\pi A}$ (17)	1460	A_{B2} (39), A_{A2} (29)
		1460	A_{A2} (52), A_{B2} (26)
4. $H^H_S H^H_S$ ($G^1 G^1$) Conformer			
37B	τ_{B2} (96)	1007A	B_{A1} (48), B_{A2} (16)
51A	τ_{A2} (89)	1056A	B_{A2} (45), B_{A1} (15)
116A	ccc (55), W_{A2} (38)	1079B	B_{B2} (20), w (18)
240A	τ_{A1} (94)	1083A	R_{A1} (38), B_{B1} (18)
241B	τ_{B1} (97)	1157B	R_{B1} (27), R_{B2} (17)
259A	W_{A1} (67), $X_{\pi A}$ (19)	1206A	t (44), $H_{\sigma A}$ (35)
294B	$X_{\pi B}$ (73), W_{B1} (11)	1239B	$H_{\sigma B}$ (71), R_{B2} (22)
339A	$X_{\pi A}$ (64), W_{A1} (17)	1279A	$H_{\sigma A}$ (53), t (27)
372B	W_{B1} (47), W_{B2} (30)	1294B	$H_{\pi B}$ (36), R_{B2} (29)
402B	W_{B2} (40), W_{B1} (28)	1341A	$H_{\pi A}$ (52), R_{A1} (19)
572A	X_A (75), W_{A1} (20)	1363B	w (49), $H_{\pi B}$ (21)
618B	X_B (90)	1382B	U_B (80)
689A	W_{A2} (34), X_A (33)	1385A	U_A (83)
849A	R_{A2} (63), R_{A1} (18)	1435A	δ (90)
887B	R_{B1} (34), r (28)	1459B	A_{B1} (64), A_{B2} (26)
920B	B_{B2} (34), r (27)	1459A	A_{A1} (85)
979B	B_{B1} (38), R_{A1} (19)	1460B	A_{B2} (65), A_{B1} (26)
		1460A	A_{A2} (85)

assigned to the $H^H_S H^H_S$ conformation: this follows from the presence of a relatively intense absorption at 150 cm^{-1} which is only assignable to this conformer. Results of calculations of the normal modes of all six isomers of *dl*-2,4-dichloropentane are given in Table I. For each isomer of 2,4-dichloropentane a band between 100 and 160 cm^{-1} is predicted. This absorption is close to 150 cm^{-1} only for the $H^H_S H^H_S$ conformer. The

Table I--(continued)

Calculated Wave Number	Potential Energy Distribution	Calculated Wave Number	Potential Energy Distribution
5. $\text{H}^{\text{13}}\text{C} \text{C}^{\text{13}}\text{H}$ (TG) conformer			
47	$\tau_{\text{B2}}(54), \tau_{\text{A2}}(37)$	1002	$\text{E}_{\text{B1}}(34), \text{F}_{\text{A1}}(19)$
52	$\tau_{\text{A2}}(48), \tau_{\text{B2}}(41)$	1064	$\text{E}_{\text{B2}}(27), \text{R}_{\text{B1}}(14)$
146	$\text{CCC}(47), \text{W}_{\text{B1}}(30)$	1094	$\text{F}_{\text{A1}}(45), \text{F}_{\text{B1}}(15)$
228	$\text{X}_{\pi\text{A}}(56)$	1119	$\text{R}_{\text{B2}}(29), \text{R}_{\text{B1}}(28)$
241	$\tau_{\text{A1}}(93)$	1149	$\text{R}_{\text{A2}}(37), \text{E}_{\text{A2}}(15)$
247	$\tau_{\text{B1}}(88)$	1206	$\text{t}(37), \text{H}_{\sigma\text{B}}(13)$
275	$\text{W}_{\text{A1}}(60)$	1241	$\text{H}_{\sigma\text{A}}(72), \text{H}_{\sigma\text{B}}(15)$
343	$\text{X}_{\pi\text{B}}(55), \text{W}_{\text{B1}}(21)$	1266	$\text{H}_{\sigma\text{B}}(55), \text{H}_{\pi\text{B}}(11)$
395	$\text{W}_{\text{A2}}(26), \text{X}_{\pi\text{A}}(15)$	1301	$\text{w}(29), \text{H}_{\pi\text{A}}(19)$
425	$\text{W}_{\text{A2}}(36), \text{W}_{\text{B2}}(17)$	1333	$\text{H}_{\pi\text{A}}(46), \text{R}_{\text{A1}}(16)$
467	$\text{W}_{\text{B2}}(49), \text{W}_{\text{B1}}(15)$	1365	$\text{U}_{\text{B}}(56), \text{R}_{\text{B1}}(17)$
614	$\text{X}_{\text{A}}(62), \text{X}_{\text{B}}(31)$	1382	$\text{U}_{\text{A}}(90)$
675	$\text{X}_{\text{B}}(47), \text{X}_{\text{A}}(35)$	1398	$\text{U}_{\text{B}}(38), \text{H}_{\pi\text{B}}(20)$
872	$\text{r}(52), \text{R}_{\text{B1}}(10)$	1429	$\delta(91)$
888	$\text{R}_{\text{A2}}(28), \text{B}_{\text{A2}}(25)$	1459	$\text{A}_{\text{A1}}(77), \text{A}_{\text{A2}}(13)$
923	$\text{B}_{\text{B2}}(24), \text{R}_{\text{B2}}(22)$	1460	$\text{A}_{\text{B2}}(67), \text{A}_{\text{B1}}(13)$
993	$\text{B}_{\text{A1}}(29), \text{B}_{\text{A2}}(26)$	1460	$\text{A}_{\text{B1}}(69), \text{A}_{\text{A2}}(13)$
		1460	$\text{A}_{\text{A2}}(57), \text{A}_{\text{B2}}(16)$
6. $\text{H}^{\text{13}}\text{C} \text{C}^{\text{13}}\text{H}$ (GG) conformer			
47B	$\tau_{\text{B2}}(96)$	1002B	$\text{E}_{\text{B1}}(29), \text{t}(18)$
57A	$\tau_{\text{A2}}(91)$	1027A	$\text{E}_{\text{A2}}(30), \text{E}_{\text{B1}}(14)$
129A	$\text{CCC}(41), \text{W}_{\text{A1}}(38)$	1115B	$\text{R}_{\text{B1}}(40), \text{R}_{\text{B2}}(18)$
217A	$\text{X}_{\pi\text{A}}(55), \text{CCC}(12)$	1123A	$\text{R}_{\text{A2}}(37), \text{R}_{\text{A1}}(23)$
241A	$\tau_{\text{A1}}(97)$	1154B	$\text{E}_{\text{B2}}(20), \text{R}_{\text{B2}}(18)$
242B	$\tau_{\text{B1}}(96)$	1217A	$\text{t}(40), \text{H}_{\pi\text{A}}(17)$
313B	$\text{W}_{\text{B1}}(81)$	1242B	$\text{H}_{\sigma\text{B}}(52)$
345A	$\text{X}_{\pi\text{A}}(87)$	1248A	$\text{H}_{\sigma\text{A}}(81)$
371A	$\text{X}_{\text{A}}(22), \text{W}_{\text{A1}}(18)$	1296B	$\text{w}(43), \text{H}_{\pi\text{B}}(37)$
418A	$\text{W}_{\text{A2}}(58), \text{W}_{\text{A1}}(25)$	1346A	$\text{H}_{\pi\text{A}}(37), \text{t}(25)$
446B	$\text{W}_{\text{B2}}(69)$	1364B	$\text{U}_{\text{B}}(57), \text{w}(17)$
627B	$\text{X}_{\text{B}}(89), \text{W}_{\text{B1}}(10)$	1381A	$\text{U}_{\text{A}}(87)$
714A	$\text{X}_{\text{A}}(71), \text{CCC}(17)$	1399B	$\text{U}_{\text{B}}(38), \text{w}(21)$
862B	$\text{r}(47), \text{R}_{\text{B1}}(26)$	1432A	$\delta(84)$
891A	$\text{R}_{\text{A2}}(28), \text{R}_{\text{A1}}(27)$	1459A	$\text{A}_{\text{A1}}(83)$
906B	$\text{E}_{\text{B2}}(23), \text{R}_{\text{B2}}(18)$	1460B	$\text{A}_{\text{B2}}(78), \text{A}_{\text{B1}}(11)$
998A	$\text{E}_{\text{A1}}(37), \text{E}_{\text{B2}}(17)$	1460B	$\text{A}_{\text{B1}}(77), \text{A}_{\text{B2}}(13)$
		1461A	$\text{A}_{\text{A2}}(80)$

^aSee Reference 8 for details concerning observed spectra.

^bSee Reference 8 for definitions of coordinates.

^cSymmetry species.

^dAssigned to small amounts of other conformers.

<u>dl FORM</u>						
CONFORMATION	TT	TG (GT)	TG' (G'T)	GG	GG' (G'G)	G'G'
STRUCTURE						
ISOMERIC STRUCTURES	S_{HH}, S_{HH}	S_{HH}, S_{CH}	$S_{HH}, S_{HH'}$	S_{CH}, S_{CH}	$S_{HH'}, S_{CH}$	$S_{HH'}, S_{HH'}$
CALCULATED FREQUENCIES	625 603 —	675 614 —	642 (615) 553	714 627 —	701 624 505	689 618 572
<u>MESO FORM</u>						
CONFORMATION	TT	TG (G'T)	TG' (GT)	GG (G'G')	GG'	G'G
STRUCTURE						
ISOMERIC STRUCTURES	S_{HH}, S_{HH}	$S_{HH}, S_{HH'}$	S_{HH}, S_{CH}	$S_{HH'}, S_{CH}$	S_{CH}, S_{CH}	$S_{HH'}, S_{HH'}$
CALCULATED FREQUENCIES	(624) 604 —	649 613 548	674 615 —	701 620 513	714 628 —	685 (626) 565

FIG. 1. Conformers of *dl*- and *meso*-2,4-dichloropentane and their calculated C-Cl stretching frequencies () indicates expected weak intensity.

elements of the Jacobian matrix, $(\partial \nu_i / \partial f_j)$, which give the sensitivity of each calculated normal frequency ν_i , to changes of each force constant (f_j), show that the frequency of the normal vibration between 100 cm^{-1} and 200 cm^{-1} in all conformers of 2,4-dichloropentane is relatively invariant with respect to minor force field adjustments. However it is apparent that this frequency is very sensitive to the geometry of the molecule.

Our results also indicate that in addition to the ${}_H S_{HC} S_H$ conformer, other minor isomers are present in measurable quantities. Weak bands at 706 cm^{-1} and 650 cm^{-1} in the spectra of crystalline and quenched samples of the *dl* stereoisomer suggest that the ${}_H S_{CH} S_H$ (GG') and ${}_H S_{HH} S_H$ (TG') forms are also present (see Fig. 1 and Table I).

Meso-2,4-dichloropentane

In the spectrum of *meso*-2,4-dichloropentane the strong absorption bands at 611 and 680 cm^{-1} are assigned to the carbon-chlorine stretching vibrations in the preferred ${}_H S_{HC} S_H$ (TG') conformation (see Table II). However, weak bands at 552 and 645 cm^{-1} suggest that other rotational isomers are present. From normal coordinate calculations, the C-Cl stretching frequencies of the ${}_H S_{HH} S_H$ (TG) isomer of *meso*-2,4-dichloropentane are predicted at 548 , 613 , and 649 cm^{-1} (see Table II). If the predicted frequency at 613 cm^{-1} (for ${}_H S_{HH} S_H$) is overlapped by the strong absorption at 611 cm^{-1} due to the dominant ${}_H S_{HC} S_H$ conformer, the observed bands at 552 cm^{-1} and 645 cm^{-1} are

explained well by admitting the presence of the ${}_{\text{H}}\text{S}_{\text{HH}}\text{S}_{\text{H}}$ form of meso-2,4-dichloropentane.

In the far infrared and Raman spectra of meso-2,4-dichloropentane there is a relatively strong band at 160 cm^{-1} which persists at low temperatures. As in the case of the absorption at 150 cm^{-1} in *dl*-2,4-dichloropentane, we were unable to assign this band to the preferred ${}_{\text{H}}\text{S}_{\text{HC}}\text{S}_{\text{H}}$ conformer. The results of normal coordinate calculations on all conformations of meso-2,4-dichloropentane (Table II) suggest that this band is uniquely assignable to a combined skeletal deformation and C-C-Cl bending mode in the ${}_{\text{H}}\text{S}_{\text{HH}}\text{S}_{\text{H}}$ conformation. A weak infrared absorption at 275 cm^{-1} in the meso spectrum is also assigned to this rotational isomer. The frequencies of the two ${}_{\text{H}}\text{S}_{\text{HH}}\text{S}_{\text{H}}$ C-Cl stretching vibrations are calculated at 604 and 625 cm^{-1} . The out-of-phase vibration at 625 cm^{-1} should be of very low intensity. The 604 cm^{-1} band is assumed to be overlapped by the strong absorption at 611 cm^{-1} of the major conformer (*viz.*, *TG'*).

Table II. Calculated Wave Number (in cm^{-1}) and Potential Energy Distribution of Conformers of meso-2,4-Dichloropentane

Observed Wave Number ^a	Calculated Wave Number	Potential Energy Distribution ^b
	1. ${}_{\text{H}}\text{S}_{\text{H}}\text{C}_{\text{H}}^{\text{S}}\text{H}$ (<i>TG'</i>) Conformer	
	49	$\tau_{\text{B}2}(82), \tau_{\text{A}2}(12)$
	56	$\tau_{\text{A}2}(75), \tau_{\text{B}2}(13)$
118	129	$\left\{ \begin{array}{l} {}_{\text{H}}\text{S}_{\text{H}}\text{H}'\text{S}_{\text{H}}^{\text{d}} \\ \text{CCC}(49), \omega_{\text{F}1}(37) \end{array} \right.$
160		$\text{H}'\text{S}_{\text{H}}\text{H}''\text{S}_{\text{H}}^{\text{d}}$
228	232	$X_{\text{TA}}(54), \tau_{\text{B}2}(22)$
	242	$\tau_{\text{A}1}(96)$
245w	245	$\tau_{\text{F}1}(73)$
275w		$\text{H}'\text{S}_{\text{H}}\text{H}''\text{S}_{\text{H}}^{\text{d}}$
315m	316	$\omega_{\text{A}1}(74)$
345w	342	$X_{\text{TB}}(51), \omega_{\text{B}1}(23)$
392w	393	$\omega_{\text{A}2}(64), X_{\text{TB}}(8)$
410ms	405	$X_{\text{TA}}(18), \text{CCC}(15)$
460w	466	$\omega_{\text{B}2}(63), \omega_{\text{B}1}(9)$
552		$\text{H}'\text{S}_{\text{H}}\text{H}'\text{S}_{\text{H}}^{\text{d}}$
611vs	615	$X_{\text{A}}(61), X_{\text{B}}(42)$
645		$\text{H}'\text{S}_{\text{H}}\text{H}'\text{S}_{\text{H}}^{\text{d}}$
680vs	674	$X_{\text{B}}(45), X_{\text{A}}(37)$
855s	861	$r(42), R_{\text{A}1}(10)$
882m	895	$R_{\text{A}2}(25), R_{\text{A}1}(21)$
926s	921	$R_{\text{F}1}(26), R_{\text{B}2}(22)$
980ms	989	$R_{\text{F}1}(31), R_{\text{A}2}(26)$
1006s	1009	$R_{\text{B}2}(40), R_{\text{A}2}(16)$
1058s	1059	$R_{\text{A}1}(32), t(13)$
1089mw	1096	$R_{\text{B}1}(27), R_{\text{A}1}(15)$
1130vs	1132	$R_{\text{F}1}(18), R_{\text{A}2}(16)$
	1145	$R_{\text{B}2}(77), R_{\text{B}2}(12)$

Table II--(continued)

Observed Wave Number ^a	Calculated Wave Number	Potential Energy Distribution ^b
1199m	1196	t(31),H _{σA} (26)
1237s	1246	H _{σB} (50),H _{σA} (35)
1272s	1271	H _{σB} (30),H _{σA} (28)
1289m	1291	w(38),H _{σA} (28)
1337mw	1335	H _{πA} (40),t(22)
1360	1365	U _B (54),R _B (17)
1378vs	1382	U _A (88)
1415vw	1398	U _B (39),H _{πB} (22)
1427w	1429	δ(91)
	1459	A _{A1} (73),A _{B2} (16)
1439s	1460	A _{B1} (69),A _{B2} (16)
1453s	1460	A _{A2} (59),A _{B2} (15)
	1460	A _{B2} (42),A _{A2} (29)

Calculated Wave Number	Potential Energy Distribution	Calculated Wave Number	Potential Energy Distribution
2. H ^S _H H ^S _H (TT) Conformer			
43A" ^c	τ _{B2} (96)	1026A'	B _{A2} (32),B _{A1} (18)
45A'	τ _{A2} (82)	1042A"	R _{B1} (41),B _{B2} (18)
153A'	ccc(52),W _{A1} (28)	1104A"	R _{B2} (22),R _{B1} (20)
223A"	X _{πB} (53),W _B (28)	1110A'	R _{A1} (57)
241A'	τ _B (96)	1160A'	R _{A2} (33),B _{A2} (16)
247A'	τ _A (92)	1185A"	t(48),H _{σB} (28)
278A'	W _A (41),X _{πA} (39)	1248A'	H _{σA} (91)
342A"	X _{πB} (42),W _{B1} (39)	1272A"	H _{πB} (35),w(29)
409A'	W _{A2} (66)	1303A"	H _{σB} (39),t(29)
450A"	W _{B2} (71),W _{B1} (21)	1328A'	H _{πA} (70),R _{A1} (16)
483A'	X _{πA} (35),ccc(24)	1359A"	U _B (41),w(27)
604A'	X _A (89)	1381A'	U _A (90)
624A"	X _B (88)	1395A"	U _B (52),R _{B2} (15)
872A'	B _{A1} (40),r(37)	1427A'	δ _A (96)
892A'	R _{A2} (35),B _{A2} (32)	1459A'	A _{A1} (72),A _{B2} (18)
935A"	R _{B1} (35),R _{B1} (23)	1460A"	A _{B1} (44),A _{A2} (44)
997A"	B _{B2} (45),B _{B1} (19)	1460A'	A _{B2} (72),A _{A1} (19)
		1460A"	A _{A2} (45),A _{B1} (45)

2,4,6-TRICHLOROHEPTANE

Even with the limitations imposed by the staggered molecular model, each isomer of 2,4,6-trichloroheptane can assume many geometrically unique forms. Thus, in this case a successful interpretation of the infrared spectra relies heavily on our ability to identify the stable structures.

Table II-(continued)

Calculated Wave Number	Potential Energy Distribution	Calculated Wave Number	Potential Energy Distribution
3. $\text{H}^{\text{SH}} \text{H}^{\text{SH}} (\text{T})$ Conformer			
40	$\tau_{\text{B2}}(96)$	1016	$\text{B}_{\text{B2}}(36), \text{B}_{\text{B1}}(17)$
53	$\tau_{\text{A2}}(89)$	1071	$\text{B}_{\text{A2}}(19), \text{F}_{\text{A1}}(13)$
123	$\text{ccc}(53), \text{X}_{\pi\text{A}}(15)$	1087	$\text{R}_{\text{B1}}(31), \text{B}_{\text{B1}}(19)$
240	$\tau_{\text{A1}}(89)$	1093	$\text{R}_{\text{A1}}(32), \text{R}_{\text{A2}}(17)$
241	$\tau_{\text{B1}}(87)$	1153	$\text{R}_{\text{B2}}(35), \text{R}_{\text{B1}}(14)$
266	$\text{W}_{\text{A1}}(51), \text{X}_{\pi\text{B}}(22)$	1199	$\text{t}(41), \text{H}_{\sigma\text{A}}(32)$
310	$\text{X}_{\pi\text{A}}(44), \text{W}_{\text{B1}}(36)$	1250	$\text{H}_{\sigma}(87)$
336	$\text{X}_{\pi\text{B}}(63), \text{W}_{\text{A1}}(17)$	1279	$\text{w}(34), \text{H}_{\pi\text{A}}(26)$
356	$\text{W}_{\text{B1}}(32), \text{X}_{\pi\text{A}}(23)$	1287	$\text{H}_{\sigma\text{A}}(50), \text{t}(29)$
420	$\text{W}_{\text{A2}}(49), \text{W}_{\text{B2}}(19)$	1323	$\text{H}_{\pi\text{B}}(49), \text{R}_{\text{B1}}(14)$
548	$\text{X}_{\text{A}}(23), \text{X}_{\text{B}}(18)$	1362	$\text{U}_{\text{A}}(30), \text{w}(29)$
613	$\text{X}_{\text{B}}(72), \text{X}_{\text{A}}(28)$	1382	$\text{U}_{\text{B}}(70), \text{U}_{\text{A}}(20)$
649	$\text{X}_{\text{A}}(50), \text{W}_{\text{A2}}(19)$	1392	$\text{U}_{\text{A}}(42), \text{w}(15)$
866	$\text{R}_{\text{A2}}(48), \text{R}_{\text{A1}}(13)$	1431	$\delta(92)$
889	$\text{r}(49), \text{B}_{\text{B1}}(15)$	1459	$\text{A}_{\text{A1}}(71), \text{A}_{\text{B2}}(12)$
920	$\text{R}_{\text{B2}}(23), \text{B}_{\text{B1}}(18)$	1460	$\text{A}_{\text{B1}}(46), \text{A}_{\text{A1}}(39)$
983	$\text{B}_{\text{A1}}(32), \text{R}_{\text{A2}}(27)$	1460	$\text{A}_{\text{A2}}(52), \text{A}_{\text{B1}}(36)$
		1460	$\text{A}_{\text{B2}}(77), \text{A}_{\text{A1}}(13)$
4. $\text{H}^{\text{SH}} \text{C}^{\text{SH}} (\text{G}^{\text{H}})$ Conformer			
45	$\tau_{\text{B2}}(52), \tau_{\text{A2}}(40)$	1000	$\text{B}_{\text{B2}}(40), \text{B}_{\text{B1}}(14)$
50	$\tau_{\text{A2}}(46), \tau_{\text{B2}}(44)$	1048	$\text{B}_{\text{A2}}(26), \text{B}_{\text{A1}}(13)$
139	$\text{ccc}(55), \text{W}_{\text{B2}}(20)$	1080	$\text{R}_{\text{A1}}(23), \text{B}_{\text{A2}}(17)$
231	$\text{X}_{\pi\text{A}}(44), \text{W}_{\text{A1}}(14)$	1130	$\text{R}_{\text{B1}}(33), \text{r}(13)$
241	$\tau_{\text{A1}}(96)$	1146	$\text{R}_{\text{B2}}(24), \text{B}_{\text{B2}}(11)$
244	$\tau_{\text{B1}}(82)$	1212	$\text{t}(39), \text{H}_{\sigma\text{B}}(14)$
304	$\text{X}_{\pi\text{B}}(36), \text{W}_{\text{A1}}(33)$	1240	$\text{H}_{\sigma\text{A}}(72), \text{H}_{\sigma\text{B}}(11)$
338	$\text{X}_{\pi\text{B}}(41), \text{W}_{\text{B1}}(29)$	1261	$\text{H}_{\sigma\text{B}}(59)$
360	$\text{X}_{\pi\text{A}}(41), \text{W}_{\text{B1}}(29)$	1314	$\text{w}(19), \text{R}_{\text{B2}}(17)$
419	$\text{W}_{\text{B2}}(41), \text{W}_{\text{A2}}(18)$	1327	$\text{H}_{\pi\text{B}}(50), \text{w}(16)$
513	$\text{X}_{\text{B}}(37), \text{W}_{\text{A2}}(31)$	1366	$\text{U}_{\text{A}}(43), \text{w}(17)$
620	$\text{X}_{\text{A}}(93), \text{W}_{\text{A1}}(12)$	1382	$\text{U}_{\text{B}}(74), \text{U}_{\text{A}}(16)$
701	$\text{X}_{\text{B}}(52), \text{ccc}(18)$	1393	$\text{U}_{\text{A}}(36), \text{H}_{\pi\text{B}}(18)$
870	$\text{R}_{\text{A2}}(28), \text{r}(19)$	1434	$\delta(85)$
879	$\text{r}(21), \text{R}_{\text{A2}}(15)$	1459	$\text{A}_{\text{A1}}(72), \text{A}_{\text{B1}}(10)$

Until recently, as in the case of 2,4-dichloropentane, rotational isomers of 2,4,6-trichloroheptane in which CH_3 groups, CH_2 and/or chlorine atoms approached one another closely were considered to be sterically forbidden. The presence of different conformations of the stereoisomers of 2,4,6-trichloroheptane can be determined in part by analyzing the C-Cl stretching vibrations of the infrared and Raman spectra, and

Table II--(continued)

Calculated Wave Number	Potential Energy Distribution	Calculated Wave Number	Potential Energy Distribution
911	$B_{B1}(31), R_{B2}(18)$	1460	$A_{B1}(47), A_{A2}(29)$
986	$B_{A1}(32), B_{A2}(21)$	1460	$A_{A2}(37), A_{B1}(29)$
		1460	$A_{B2}(57), A_{A2}(23)$

5. $H^S H^I, H^I S^H$ (G'G) Conformer

38A''	$\tau_{B2}(97)$	1007A'	$F_{A1}(49), H_{\pi A}(13)$
46A'	$\tau_{A2}(85)$	1029A''	$R_{B1}(33), R_{B1}(29)$
121A'	$CCC(55), W_{A2}(37)$	1068A'	$F_{A2}(51), R_{A2}(11)$
231A''	$X_{\pi B}(41), \tau_{B1}(30)$	1133A'	$R_{A1}(39), B_{A1}(16)$
241A'	$\tau_{A1}(96)$	1139A''	$w(20), H_{\pi B}(14)$
246A''	$\tau_{B1}(65), W_{B1}(18)$	1199A''	$t(40), H_{\sigma B}(34)$
305A''	$W_{B1}(56), X_{\pi B}(34)$	1249A'	$H_{\sigma A}(89)$
339A'	$X_{\pi A}(59), W_{A1}(22)$	1262A''	$R_{B2}(31), t(22)$
389A'	$W_{A1}(59), X_{\pi A}(22)$	1312A''	$H_{\sigma B}(28), R_{B2}(17)$
396A'	$W_{B2}(71)$	1329A'	$H_{\pi A}(61), R_{A2}(18)$
565A'	$X_A(78), W_{A1}(11)$	1367A''	$w(43), H_{\pi R}(27)$
626A''	$X_B(89)$	1382A''	$U_B(82)$
685A'	$W_{A2}(35), X_A(28)$	1385A'	$U_A(84)$
851A'	$R_{A2}(59), R_{A1}(21)$	1435A'	$\delta(92)$
897A''	$R_{B1}(29), B_{B1}(27)$	1459A'	$A_{B1}(71), A_{A2}(18)$
902A'	$r(50), B_{A2}(21)$	1459A''	$A_{A1}(80)$
997A''	$B_{B2}(55), B_{B1}(19)$	1460A''	$A_{B2}(81)$
		1460A'	$A_{A2}(72), A_{B1}(19)$

6. $H^S C^S, C^S H^I$ (GG') Conformer

55A'	$\tau_{A2}(88)$	1017A''	$B_{B2}(42), R_{B1}(27)$
56A''	$\tau_{B2}(96)$	1021A'	$B_{A2}(52), B_{A1}(14)$
137A'	$CCC(36), W_{A1}(29)$	1116A''	$R_{B2}(31), R_{B1}(23)$
225A'	$X_{\pi A}(46), CCC(15)$	1123A'	$R_{A1}(40), R_{A2}(22)$
241A''	$\tau_{B1}(98)$	1149A'	$R_{A2}(20), B_{A1}(16)$
248A'	$\tau_{A1}(84)$	1213A''	$t(34), w(14)$
274A''	$W_{B1}(89)$	1245A''	$H_{\sigma B}(85)$
346A''	$X_{\pi B}(88)$	1247A'	$H_{\sigma A}(90)$
370A'	$W_{A2}(22), X_A(21)$	1321A'	$H_{\pi A}(63), R_{A1}(17)$
438A'	$W_{A2}(44), W_{A1}(31)$	1322A''	$w(47), t(23)$

by means of NMR. In addition, the probable geometry assumed by adjacent carbon-chlorine bonds in 2,4,6-trichloroheptane can be obtained from knowledge of this relative orientation in 2,4-dichloropentane. We have calculated the normal vibration frequencies of the $H^S H^H H^H S^H$ (TTTT) and $H^S H^H S^C C^S H^I$ (TTGG) conformers of syndiotactic 2,4,6-trichloroheptane. For the isotactic isomer the $H^S H^C S^H C^S H^I$ (TGTG), $H^S C^H S^H C^S H^I$

Table 11--(concluded)

Calculated Wave Number	Potential Energy Distribution	Calculated Wave Number	Potential Energy Distribution
440A ^a	$W_{B2}(78)$	1369A ^a	$U_B(67), R_{B1}(17)$
628A ^a	$X_B(89)$	1382A ^a	$U_A(89)$
714A ^a	$X_A(71), CCC(17)$	1400A ^a	$U_B(28), H_{TP}(24)$
866A ^a	$r(45), R_{A1}(29)$	1431A ^a	$\delta(87)$
898A ^a	$R_{B1}(26), R_{B2}(25)$	1459A ^a	$A_{A1}(81)$
898A ^a	$B_{A1}(43), R_{A2}(21)$	1460A ^a	$A_{A2}(84)$
989A ^a	$B_{B1}(41), B_{B2}(21)$	1460A ^a	$A_{B1}(83)$
		1461A ^a	$A_{B2}(79)$

^aSee Reference 8 for details concerning observed spectra.

^bSee Reference 8 for definitions of coordinates.

^cSymmetry species.

^dAssigned to small amounts of other conformers.

(*G'TTG*), ${}_H S_{HH} S_{HH} S_H$ (*TTTG'*), and the ${}_H S_{HH} S_{HH} S_H$ (*TTTT*) conformers were all considered. The spectrum of heterotactic 2,4,6-trichloroheptane is well accounted for by two conformations, ${}_H S_{HH} S_{HC} S_H$ (*TTTG*) and ${}_H S_{HH} S_{CH} S_H$ (*TTG'T*). The observed and calculated frequencies for 2,4,6-trichloroheptane are given in Tables III, IV, and V. The infrared spectra for 2,4,6-trichloroheptane were reported by Shimanouchi, Tasumi, and Abe (*6*) and by Doskočilova, *et al.* (*11*). The observed spectra used here are a combination of these observations.

The C-Cl stretching region of the spectrum reported by Doskočilova *et al.*, for the syndiotactic form of 2,4,6-trichloroheptane contains a strong band at 608 cm^{-1} which decreases in intensity at low temperature and develops a shoulder at 604 cm^{-1} , and a strong band at 642 cm^{-1} which shifts to 632 cm^{-1} and increases in intensity as the sample solidifies. No bands were reported in the region of ${}_C S_H$ type C-Cl stretching vibrations. For syndiotactic 2,4,6-trichloroheptane, C-Cl stretching frequencies were calculated at 604 cm^{-1} , 616 cm^{-1} , and 629 cm^{-1} for the ${}_H S_{HH} S_{HH} S_H$ (*TTTT*) conformer and at 610 cm^{-1} , 631 cm^{-1} , and 722 cm^{-1} for the ${}_H S_{HH} S_{CC} S_H$ (*TTGG*) form. The observed bands are assigned as follows: the band at 604 cm^{-1} is assigned to the predicted band at 604 cm^{-1} ; the band at 608 cm^{-1} is assigned to the overlapped C-Cl stretching vibrations calculated at 616 cm^{-1} for the all trans ${}_H S_{HH} S_{HH} S_H$ conformer and at 610 cm^{-1} for the ${}_H S_{HH} S_{CC} S_H$ conformer; the 632 cm^{-1} band is assigned to the predicted 629 cm^{-1} band in ${}_H S_{HH} S_{HH} S_H$ conformer and to the 631 cm^{-1} band of the ${}_H S_{HH} S_{CC} S_H$ conformation. Although not reported as such, some weak absorption in the region 725 cm^{-1} can be observed in the spectrum of syndiotactic 2,4,6-trichloroheptane recorded by Doskočilova *et al.* This is assignable to the ${}_C S_H$ C-Cl stretching vibration of the ${}_H S_{HH} S_{CC} S_H$ isomer, which is calculated at 722 cm^{-1} .

The region of the C-Cl stretching vibrations in the spectrum of isotactic 2,4,6-trichloroheptane contains strong bands at 619 cm^{-1} and 688 cm^{-1} . At elevated temperatures a shoulder at 635 cm^{-1} is present which disappears at low temperatures. There

Table III. Observed and Calculated Wave Numbers (in cm^{-1}) and Potential Energy Distributions of Syndiotactic 2,4,6-Trichloroheptane

Observed Wave Number	Calculated Wave Number	Potential Energy Distribution ^b
$\begin{matrix} \text{H}^{\text{S}}\text{H} & \text{H}^{\text{S}}\text{H} & \text{H}^{\text{S}}\text{H} \\ (\text{TTTT}) \end{matrix}$	$\begin{matrix} \text{H}^{\text{S}}\text{H} & \text{H}^{\text{S}}\text{C} & \text{C}^{\text{S}}\text{H} \\ (\text{TTGG}) \end{matrix}$	
24		$\tau_3(25), \tau_4(25), \tau_5(22), \tau_2(22)$
	25	$\tau_3(62), \tau_2(25)$
31		$\tau_3(40), \tau_4(40)$
	32	$\tau_5(53), \tau_4(27)$
42		$\tau_2(40), \tau_5(40)$
	51	$\tau_5(26), W_{12}(16), \tau_2(13), \tau_4(11)$
	61	$\tau_4(41), \tau_2(37)$
81		$W_{12}(30), \text{ccc}_1(22), \text{ccc}_2(22)$
82		$\tau_3(21), \tau_4(21), \tau_2(20), \tau_5(20)$
	117	$\text{ccc}_1(29), \bar{w}_{12}(15)$
	128	$\text{ccc}_2(25), X_{\pi 2}(20)$
129		$X_{\pi 2}(23), \text{ccc}_1(19), \text{ccc}_2(19)$
	212	$X_{\pi 3}(33), X_{\pi 2}(15)$
227		$X_{\pi 1}(20), X_{\pi 2}(20), \bar{w}_{12}(13)$
	237	$\tau_6(78)$
239		$\tau_1(46), \tau_2(46)$
	242	$\tau_1(89)$
243		$\tau_1(44), \tau_2(44)$
	271	$W_{11}(20), \bar{w}_{13}(15), \tau_6(12)$
289		$X_{\pi 2}(33), W_{11}(21), \bar{w}_{13}(21)$
	316	$W_{11}(27), W_{12}(21), \bar{w}_{13}(14)$
319		$W_{11}(30), \bar{w}_{13}(30), W_{12}(16)$
335		$X_{\pi 1}(29), X_{\pi 3}(29), X_{\pi 2}(12)$
	340	$X_{\pi 1}(47), X_{\pi 3}(11)$
	357	$X_{\pi 3}(19), W_{21}(13), W_{13}(12)$
363		$W_{22}(35), W_{23}(12), W_{21}(12), W_{12}(12)$
	369	$W_{21}(25), W_{22}(21), X_{\pi 3}(13)$
395		$X_{\pi 1}(20), X_{\pi 3}(20)$
396		$W_{21}(31), W_{23}(31)$
	430	$W_{23}(47), W_{13}(13)$
	461	$W_{21}(33), W_{22}(26)$
480	479	$W_{22}(29), W_{21}(14), W_{23}(14)$
	499	$\text{ccc}_1(19), X_{\pi 2}(11)$
561	555	$\text{ccc}_2(17), \text{ccc}_1(17), X_{\pi 2}(13)$
604sh	604	$X_2(33), X_1(20), X_3(20)$

is also a band at approximately 563 cm^{-1} which has a similar temperature dependence. The predicted $\text{H}_\text{S}\text{H}$ C-Cl stretching vibrations for the $\text{H}_\text{S}\text{H}_\text{C}\text{S}_\text{H}\text{C}\text{S}_\text{H}$ and $\text{H}_\text{S}\text{C}_\text{H}\text{S}_\text{H}\text{C}\text{S}_\text{H}$ isomers are at 614 cm^{-1} and 619 cm^{-1} , respectively. These are jointly assigned to the observed band at 619 cm^{-1} . The four $\text{C}_\text{S}\text{H}$ C-Cl stretching vibrations are predicted at

Table III--(continued)

Observed Wave Number	Calculated Wave Number		Potential Energy Distribution
	$\text{H}^{\text{S}}\text{H} \quad \text{H}^{\text{S}}\text{H} \quad \text{H}^{\text{S}}\text{H}$ (TTT)	$\text{H}^{\text{S}}\text{H} \quad \text{H}^{\text{S}}\text{C} \quad \text{C}^{\text{S}}\text{H}$ (TTG)	
608s		610	$X_1(62)$
	616		$X_1(34), X_3(34)$
632s	629		$X_2(38), X_1(16), X_3(16)$
		631	$X_3(37), X_2(26)$
725w		722	$X_2(26), X_3(22), \text{CCO}_2(14)$
858m		853	$r_2(41)$
	855		$r_1(32), r_2(32)$
880vw		888	$r_1(26), B_{21}(11)$
888	892		$R_2(18), R_5(18), B_{11}(15), B_{12}(15)$
		899	$r_1(17), R_6(15), R_5(13)$
918	909		$r_2(13), r_1(13), B_{21}(12), B_{22}(12)$
		926	$B_{11}(23), R_2(21)$
932s	938		$B_{12}(13), B_{11}(13), R_2(11), R_5(11)$
		978	$R_3(16), B_{21}(14)$
974s	994		$B_{22}(11), B_{21}(11)$
	998		$B_{21}(25), B_{22}(25)$
1012* <i>m</i>		1010	$B_{22}(41), B_{12}(23)$
1020wsh		1017	$B_{21}(28)$
1054s	1063		$B_{21}(13), B_{22}(13)$
1074*	1075		$R_1(14), R_6(14)$
		1078	$R_1(34)$
1105 <i>m</i>	1101		$H_{\sigma 2}(15), R_6(12), R_1(12)$
	1101		$R_1(15), R_6(15), R_4(12), R_3(12)$
		1106	$t_1(17), R_6(14)$
		1108	$R_4(35), R_1(14), R_3(13)$
		1124	$R_5(25), R_6(15), H_{\pi 3}(12)$
1119s	1125		$R_3(11), R_4(11)$
1144vs	1136		$R_2(17), R_5(17)$
		1136	$R_2(22), R_3(15)$
1168s	1167		$t_1(17), t_2(17), H_{\pi 2}(14)$
		1177	$t_1(20)$
1186s	1188		$H_{\sigma 2}(17), t_1(11), t_2(11)$
1225msh		1212	$t_2(27), H_{\sigma 2}(12)$
1240msh		1246	$H_{\sigma 3}(79)$
		1251	$H_{\sigma 1}(37), H_{\sigma 2}(37)$

Table III--(concluded)

Observed Wave Number	Calculated Wave Number		Potential Energy ^b Distribution
	H ^S H H ^S H H ^S H (TTTT)	H ^S H H ^S C C ^S H (TTGG)	
1253s	1256		H _{σ1} (28), H _{σ3} (28), H _{σ2} (24)
1265vs	1257		H _{π2} (25), w ₁ (22), w ₂ (22)
1274m	1273		H _{σ1} (29), H _{σ3} (29)
		1282	w ₁ (28), H _{π2} (13), w ₂ (11)
		1283	H _{σ1} (21), t ₁ (14), H _{π1} (14), H _{π2} (14)
1298*vw	1293		H _{π3} (17), H _{π1} (17), w ₂ (13), w ₁ (13)
1305vwsh	1312	1309	t ₁ (20), w ₂ (20)
			t ₁ (21), t ₂ (21), H _{σ2} (21)
			H _{π1} (20), H _{π3} (20), H _{π2} (15)
1317m	1322	1338	t ₂ (17), H _{π1} (15), H _{π3} (12)
		1358	U ₂ (16), w ₂ (11)
			U ₁ (15), U ₂ (15), w ₁ (14), w ₂ (14)
1355vwsh	1362	1369	U ₁ (21), U ₂ (21), H _{π2} (12)
			U ₁ (27), U ₂ (27)
		1373	U ₁ (27), U ₂ (27)
		1388	U ₁ (34), U ₂ (26)
1380s	1390		U ₁ (18), U ₂ (18)
		1393	U ₁ (18), U ₂ (18)
		1397	w ₂ (14), U ₂ (13)
1422m	1424		δ ₁ (46), δ ₂ (46)
		1426	δ ₁ (90)
	1429		δ ₁ (47), δ ₂ (47)
		1434	δ ₂ (77)
	1459		A ₁₁ (39), A ₂₂ (39)
	1459		A ₂₂ (36), A ₁₁ (36)
	1459		A ₁₂ (43), A ₂₁ (43)
	1448s	1459	
1459			A ₁₁ (69), A ₂₁ (18)
1459			A ₁₂ (73), A ₂₂ (15)
1459			A ₂₁ (72), A ₁₁ (19)
1460			A ₂₂ (72), A ₁₂ (16)

* Also assigned to the heterotactic stereoisomers.

^a References 6 and 11.

^b See Reference 8 for definitions of coordinates.

Table IV. Observed and Calculated Wave Numbers (in cm^{-1}) and Potential Energy Distributions of Isotactic 2,4,6-Trichloroheptane

Observed Wave Number ^a	Calculated Wave Number		Potential Energy ^b Distribution
	$\text{H}^{\text{S}}\text{H} \quad \text{C}^{\text{S}}\text{H} \quad \text{C}^{\text{C}}\text{H}$ (TGTG)	$\text{H}^{\text{S}}\text{C} \quad \text{H}^{\text{S}}\text{H} \quad \text{C}^{\text{C}}\text{H}$ (GTTG)	
	24		$\tau_3(41), \tau_2(38), \tau_5(12)$
		31	$\tau_2(25), \tau_5(25), \tau_3(23), \tau_4(23)$
	32		$\tau_4(59), \tau_5(25)$
		35	$\tau_3(34), \tau_4(34)$
		46	$\tau_2(36), \tau_5(36)$
	52		$\tau_2(30), \tau_4(16), w_{12}(16), \tau_5(12)$
	61		$\tau_3(41), \tau_5(34)$
		70	$w_{12}(28), \text{ccc}_1(20), \text{ccc}_2(20)$
		78	$\tau_3(23), \tau_4(23), \tau_2(16), \tau_5(16)$
	105		$\text{ccc}_1(22), w_{12}(18)$
	137		$\text{ccc}_2(31), x_{\pi 2}(24), \text{ccc}_1(13), w_{13}(11)$
		153	$x_{\pi 2}(21), \text{ccc}_1(17), \text{ccc}_2(17)$
		169	$x_{\pi 1}(22), x_{\pi 3}(22)$
	223		$x_{\pi 2}(19), x_{\pi 3}(17), \tau_6(12)$
		235	$\tau_1(37), \tau_6(37)$
	239		$\tau_6(46), \tau_1(43)$
		240	$\tau_1(47), \tau_6(47)$
	247		$\tau_6(35), \tau_1(33)$
	256		$w_{11}(23), x_{\pi 3}(22)$
		266	$x_{\pi 2}(19), x_{\pi 1}(15), x_{\pi 3}(15)$
	310		$w_{12}(31), w_{13}(24)$
		316	$w_{11}(30), w_{13}(30), w_{12}(20)$
		335	$x_{\pi 3}(24), x_{\pi 1}(24), w_{11}(13), w_{13}(13)$
	338		$w_{11}(26), x_{\pi 3}(24), w_{13}(19)$
		361	$w_{12}(16), w_{22}(16), x_{\pi 1}(11), x_{\pi 2}(11)$
	376		$w_{21}(22), x_{\pi 1}(16)$
	384		$w_{22}(14), x_{\pi 2}(12), w_{13}(11), x_{\pi 1}(11)$
		387	$w_{22}(23), w_{21}(15), w_{23}(15)$
	411		$w_{21}(18), x_2(15), x_{\pi 1}(14), w_{22}(12)$
425w		424	$w_{21}(30), w_{23}(30)$
450w	440		$w_{23}(34)$
		472	$x_{\pi 2}(23), x_1(16), x_2(16), \text{ccc}_1(14), \text{ccc}_2(14)$
		483	$w_{22}(27), w_{21}(16), w_{23}(16)$
495m	497		$w_{22}(21), w_{21}(14)$

Table IV--(continued)

Observed Wave Number	Calculated Wave Number		Potential Energy Distribution
	$\text{H}^{\text{S}}\text{H} \text{C}^{\text{S}}\text{H} \text{C}^{\text{S}}\text{H}$ (TGTG)	$\text{H}^{\text{S}}\text{C} \text{H}^{\text{S}}\text{H} \text{C}^{\text{S}}\text{H}$ (G'TTG)	
563vw			$\text{H}^{\text{S}}\text{H} \text{H}^{\text{S}}\text{H} \text{H}^{\text{S}}\text{H} \text{C}$
619s	614		$X_1(71)$
		619	$X_2(70)$
635sh			$\text{H}^{\text{S}}\text{H} \text{H}^{\text{S}}\text{H} \text{H}^{\text{S}}\text{H} \text{C}$
	664		$X_3(41), X_2(21)$
		666	$X_1(32), X_2(32)$
		689	$X_1(25), X_3(25)$
688s	699		$X_2(34), X_3(17)$
		845	$r_1(29), r_2(29)$
852m	852		$r_1(36), r_2(11)$
887m	884		$r_2(25)$
		894	$B_{12}(12), B_{11}(12), R_2(11), R_5(11)$
896m		899	$R_1(19), R_6(19)$
	910		$B_{12}(20), B_{22}(18), R_5(12)$
916m	917		$B_{11}(26), R_2(24)$
		920	$r_1(13), r_2(13)$
972m	978		$B_{21}(37), R_4(13)$
984m		1001	$B_{21}(25), B_{22}(25)$
998m		1005	$B_{12}(15), B_{22}(15), B_{11}(14), B_{12}(14)$
1018	1008		$B_{22}(42), B_{12}(20)$
1030m	1033		$t_2(12), R_4(12)$
1044m		1041	$R_3(13), R_4(13)$
		1042	$B_{11}(11), B_{12}(11)$
1071w	1071		$R_1(19), R_6(11)$
1080m	1085		$R_1(17), R_3(17), B_{21}(15)$
		1089	$R_3(20), R_4(20)$
1108m	1114		$R_3(20), R_1(18)$
1123s		1121	$R_1(11), R_6(11)$
		1133	$R_2(12), R_5(12)$
	1134		$R_5(25), H_{\pi 3}(14), R_6(14)$
		1135	$R_2(18), R_5(18)$
	1142		$R_2(20), B_{11}(16), R_4(14)$
1175vw	1181		$t_1(26), H_{\pi 2}(12)$
		1187	$H_{\sigma 2}(30), t_1(13), t_2(13)$
1190m	1195		$H_{\sigma 2}(30), t_2(22)$
1203m		1205	$t_1(20), t_2(20)$

Table IV--(continued)

Observed Wave Number	Calculated Wave Number		Potential Energy Distribution
	$\text{H}^{\text{S}}\text{H} \quad \text{C}^{\text{S}}\text{H} \quad \text{O}^{\text{S}}\text{H}$ (GTTG)	$\text{H}^{\text{S}}\text{C} \quad \text{H}^{\text{S}}\text{H} \quad \text{C}^{\text{S}}\text{H}$ (G'TTG)	
1233s		1243	$\text{H}_{\pi 1}(36), \text{H}_{\sigma 3}(36)$
1243s	1247		$\text{H}_{\sigma 3}(76)$
		1249	$\text{H}_{\pi 1}(39), \text{H}_{\sigma 3}(39)$
1252s	1262		$\text{H}_{\sigma 1}(35), \text{H}_{\sigma 2}(25)$
		1265	$\text{H}_{\sigma 2}(28), \text{w}_1(19), \text{w}_2(19)$
1277m	1268		$\text{H}_{\sigma 2}(21), \text{H}_{\sigma 1}(17), \text{w}_2(11)$
		1281	$\text{H}_{\sigma 2}(42)$
1288m	1290		$\text{H}_{\pi 1}(28), \text{w}_1(25)$
1312m	1311		$\text{w}_2(26), \text{t}_1(17), \text{H}_{\pi 1}(11)$
		1328	$\text{t}_2(15), \text{t}_1(15), \text{w}_1(14), \text{w}_2(14)$
		1332	$\text{H}_{\pi 1}(16), \text{H}_{\pi 3}(16)$
1334w	1336		$\text{H}_{\pi 3}(17), \text{t}_2(15), \text{H}_{\pi 2}(11)$
1353w	1357		$\text{w}_1(14), \text{u}_2(13), \text{u}_1(11)$
		1364	$\text{u}_2(21), \text{u}_1(21)$
		1371	$\text{u}_1(27), \text{u}_2(27)$
	1374		$\text{u}_2(31), \text{u}_1(31)$
1385s	1388		$\text{u}_1(32), \text{u}_2(32)$
		1392	$\text{u}_1(22), \text{u}_2(22)$
		1395	$\text{u}_1(13), \text{u}_2(13), \text{H}_{\pi 2}(11)$
1415vw	1399		$\text{w}_1(11), \text{w}_2(11)$
		1427	$\delta_1(45), \delta_2(45)$
	1428		$\delta_2(70), \delta_1(18)$
1430msh		1430	$\delta_2(45), \delta_1(45)$
	1431		$\delta_1(65), \delta_2(19)$
1447s	1459		$\text{A}_{11}(59), \text{A}_{12}(16), \text{A}_{21}(11)$
	1459		$\text{A}_{12}(57), \text{A}_{11}(15), \text{A}_{22}(12)$
		1459	$\text{A}_{11}(36), \text{A}_{21}(36)$
		1459	$\text{A}_{21}(39), \text{A}_{11}(39)$
	1459		$\text{A}_{21}(75), \text{A}_{11}(16)$
	1460		$\text{A}_{22}(74), \text{A}_{12}(16)$
		1460	$\text{A}_{22}(73)$
		1460	$\text{A}_{12}(69)$

Table IV--(continued)

Observed Wave Number	Calculated Wave Number		Potential Energy Distribution
	$\text{H}^{\text{S}}\text{H} \text{H}^{\text{S}}\text{H} \text{H}^{\text{S}}\text{H}$ (TTTG')	$\text{H}^{\text{S}}\text{H} \text{H}^{\text{S}}\text{H} \text{H}^{\text{S}}\text{H}$ (TTTT)	
	23		$\tau_4(37), \tau_2(28), \tau_5(19)$
		25	$\tau_3(24), \tau_2(24), \tau_4(24), \tau_5(24)$
		31	$\tau_3(42), \tau_2(42)$
	31		$\tau_3(55), \tau_4(30)$
		38	$\tau_2(36), \tau_5(36)$
	43		$\tau_5(43), \tau_2(39)$
	60		$\tau_5(17), \tau_4(16), \tau_3(16), \text{ccc}_1(13)$
		63	$\tau_3(19), \tau_4(19), \tau_2(16), \tau_5(16)$
	88		$\text{ccc}_2(32), \text{w}_{12}(16)$
		92	$\text{ccc}_1(21), \text{ccc}_2(21), \text{w}_{12}(19)$
	162		$\text{ccc}_1(22), \text{x}_{\pi 2}(15), \text{ccc}_2(11)$
		194	$\text{w}_{12}(32), \text{x}_{\pi 3}(22), \text{x}_{\pi 1}(22)$
		201	$\text{ccc}_1(17), \text{ccc}_2(17), \text{w}_{13}(13), \text{w}_{11}(13)$
		210	$\text{x}_{\pi 2}(60)$
	213		$\text{x}_{\pi 1}(34), \text{w}_{12}(28)$
	233		$\text{x}_{\pi 2}(37), \text{w}_{11}(18)$
	242		$\tau_6(88)$
		243	$\tau_1(48), \tau_6(48)$
	244		$\tau_1(89)$
		246	$\tau_1(45), \tau_6(45)$
		279	$\text{w}_{13}(32), \text{w}_{11}(32)$
	315		$\text{x}_{\pi 1}(26), \text{w}_{11}(23), \text{w}_{13}(22)$
		325	$\text{x}_{\pi 1}(26), \text{x}_{\pi 3}(26), \text{w}_{11}(17), \text{w}_{13}(17)$
	331		$\text{x}_{\pi 3}(65)$
	358		$\text{w}_{13}(33), \text{w}_{23}(15)$
		392	$\text{w}_{23}(16), \text{w}_{21}(16)$
	411		$\text{w}_{21}(40), \text{w}_{22}(23)$
		417	$\text{w}_{21}(32), \text{w}_{23}(32)$
		429	$\text{w}_{22}(34)$
	444		$\text{w}_{22}(30), \text{w}_{21}(24)$
	457		$\text{x}_{\pi 1}(20), \text{ccc}_1(16), \text{w}_{23}(11)$
		469	$\text{w}_{22}(21), \text{w}_{21}(15), \text{w}_{23}(15)$
	568		$\text{x}_3(43)$
		565	$\text{ccc}_1(19), \text{ccc}_2(19), \text{x}_{\pi 2}(16)$
		604	$\text{x}_2(36), \text{x}_1(20), \text{x}_3(20)$

Table IV--(continued)

Observed Wave Number	Calculated Wave Number	Potential Energy Distribution
	$\text{H}^{\text{S}}\text{H} \text{H}^{\text{S}}\text{H} \text{H}^{\text{S}}\text{H}$ (TTTG')	$\text{H}^{\text{S}}\text{H} \text{H}^{\text{S}}\text{H} \text{H}^{\text{S}}\text{H}$ (TTTT)
	607	$X_1(45), X_2(31)$
		613 $X_3(36), X_1(36)$
	623	$X_2(40), X_1(29)$
		628 $X_2(37), X_1(16), X_3(16)$
	660	$X_3(38), W_{23}(19), \text{ccc}_2(12)$
		862 $r_1(35), r_2(27)$
	865	$r_1(30), r_2(30)$
	883	$R_5(25), R_6(16)$
		893 $R_2(19), R_5(19), B_{11}(15), B_{21}(15)$
		912 $B_{12}(14), B_{22}(14), r_1(11), r_2(11)$
	921	$B_{11}(23), R_2(16)$
	932	$r_2(25), r_1(16)$
		941 $B_{11}(14), B_{21}(14)$
	970	$R_{22}(35), R_4(16), H_{\pi 3}(13)$
		1003 $B_{12}(26), B_{22}(26)$
		1011 $R_3(16), R_4(16), R_1(16), R_6(16)$
	1013	$B_{12}(40)$
		1027 $B_{12}(18), B_{22}(18)$
	1031	$B_{22}(18), R_1(14)$
	1071	$B_{12}(27), R_6(12)$
		1071 $R_6(17), R_1(17)$
	1075	$R_3(23), R_4(16)$
		1092 $R_4(25), R_3(25)$
	1100	$R_1(38)$
		1105 $R_1(20), R_6(20)$
		1113 $R_1(12), R_6(12), R_2(11), R_5(11)$
	1121	$R_2(19), B_{11}(14), R_3(12)$
	1146	$R_6(20), R_4(18), R_5(15)$
		1154 less than 10%
		1183 $t_1(25), t_2(25)$
	1185	$t_1(41), R_2(14), H_{\sigma 1}(11)$
		1186 $t_2(20), t_1(20), H_{\sigma 2}(20)$
	1192	$t_2(31), H_{\sigma 2}(16), H_{\sigma 3}(12)$
	1243	$H_{\sigma 1}(26), H_{\sigma 2}(15)$
		1245 $H_{\sigma 1}(19), H_{\sigma 3}(19), H_{\sigma 2}(16)$

Table IV--(concluded)

Observed Wave Number	Calculated Wave Number		Potential Energy Distribution
	$\overset{\text{H}}{\text{C}}\overset{\text{H}}{\text{H}}\overset{\text{H}}{\text{C}}\overset{\text{H}}{\text{H}}\overset{\text{H}}{\text{C}}\overset{\text{H}}{\text{H}}$ (TTGT ^a)	$\overset{\text{H}}{\text{S}}\overset{\text{H}}{\text{H}}\overset{\text{S}}{\text{H}}\overset{\text{H}}{\text{S}}\overset{\text{H}}{\text{H}}\overset{\text{S}}{\text{H}}$ (TTTT)	
		1247	$H_{\sigma 1}(20), H_{\sigma 3}(20), H_{\sigma 2}(14)$
	1257		$H_{\sigma 3}(40), H_{\pi 2}(14), w_1(11)$
	1268		$H_{\sigma 1}(26), t_2(14), H_{\sigma 3}(11)$
		1282	$H_{\sigma 3}(20), H_{\pi 1}(20), t_1(11),$ $t_2(11),$
		1294	$H_{\pi 1}(21), H_{\pi 2}(21), w_1(10),$ $w_2(10),$
	1305		$H_{\sigma 2}(18), H_{\pi 1}(17), t_1(14)$
	1309		$H_{\pi 1}(18), w_1(11)$
		1316	$H_{\sigma 2}(24), t_1(16), t_2(16)$
		1327	$H_{\pi 1}(23), H_{\pi 3}(23), H_{\pi 2}(19)$
	1336		$H_{\pi 3}(29), t_2(11)$
		1360	$U_1(14), U_2(14), w_2(14), w_1(14)$
	1360		$w_1(22), U_1(20), w_2(12)$
		1366	$H_{\pi 2}(16), U_1(15), U_2(15)$
	1370		$w_2(22), H_{\pi 2}(17), R_4(12)$
	1383		$U_2(70)$
		1389	$U_2(28), U_1(28)$
		1390	$U_1(24), U_2(24)$
	1390		$U_1(50), w_1(11)$
		1425	$\delta_1(47), \delta_2(47)$
	1426		$\delta_1(81), \delta_2(13)$
		1428	$\delta_1(47), \delta_2(47)$
	1431		$\delta_2(78), \delta_1(13)$
	1459		$A_{11}(60), A_{12}(19)$
		1459	$A_{22}(65), A_{21}(18)$
	1459		$A_{21}(66)$
		1459	$A_{11}(34), A_{21}(34)$
	1459		$A_{22}(76), A_{21}(15)$
		1459	$A_{12}(60), A_{11}(23)$
	1459		$A_{12}(69), A_{11}(22)$
		1459	$A_{21}(34), A_{11}(34)$

^a References 6 and 11.

^b See Reference 8 for definitions of coordinates.

^c Assigned to another conformer.

Table V. Observed and Calculated Wave Numbers (in cm^{-1}) and Potential Energy Distributions of Heterotactic 2,4,6-Trichloroheptane

Observed Wave Number ^a	Calculated Wave Number		Potential Energy Distribution ^b
	$\text{H}^{\text{S}}\text{H} \ \text{H}^{\text{S}}\text{H} \ \text{C}^{\text{S}}\text{H}$ (TTT)	$\text{H}^{\text{S}}\text{H} \ \text{H}^{\text{S}}\text{C} \ \text{H}^{\text{S}}\text{H}$ (TGT)	
		25	$\tau_4(32), \tau_2(31), \tau_3(16), \tau_5(15)$
		25	$\tau_3(47), \tau_5(31)$
	26		$\tau_3(49), \tau_5(21), \tau_2(18)$
	34		$\tau_4(54), \tau_2(15)$
	45		$\tau_5(44), \tau_2(34)$
		58	$\tau_2(50), \tau_4(17)$
		59	$\tau_5(34), \tau_4(27)$
	73		$W_{12}(22), \text{CCC}_2(18), \text{CCC}_1(16), \tau_4(11)$
	83		$\tau_3(17), \tau_2(15), \tau_5(11)$
		105	$\text{CCC}_1(21), W_{12}(18), \text{CCC}_2(14)$
		130	$\text{CCC}_2(22), X_{\pi 2}(20), \text{CCC}_1(19)$
	139		$X_{\pi 2}(21), \text{CCC}_1(19), \text{CCC}_2(16),$ $X_{\pi 1}(12), W_{13}(12)$
	207		$X_{\pi 3}(31)$
		233	$\tau_1(24), X_{\pi 2}(22), \tau_6(12), X_{\pi 3}(12)$
	238		$\tau_6(83)$
		239	$\tau_6(65), \tau_1(26)$
	241		$\tau_1(87)$
		246	$\tau_1(46), \tau_6(13), X_{\pi 3}(14)$
		271	$X_{\pi 1}(20), W_{13}(19), W_{11}(14)$
	281		$W_{11}(22), X_{\pi 2}(21), W_{13}(15)$
		314	$W_{11}(31), W_{12}(22)$
	316		$W_{11}(27), W_{13}(19), W_{12}(18)$
	335		$X_{\pi 3}(29), X_{\pi 1}(24), W_{13}(14)$
		338	$W_{13}(35), X_{\pi 1}(28)$
		362	$W_{21}(34), W_{22}(17), W_{11}(13)$
	366		$W_{22}(31), W_{12}(14), X_{\pi 1}(12)$
	374		$W_{21}(31), X_{\pi 3}(11)$
		394	$X_{\pi 3}(31), X_{\pi 1}(14)$
		409	$W_{23}(38)$
	415		$W_{23}(36), W_{21}(18), W_{13}(11)$
460m		461	$W_{21}(32), W_{22}(25)$
480m	480		$W_{22}(28), W_{23}(18), W_{21}(11)$
		514	$W_{23}(14), \text{CCC}_1(13)$

Table V--(continued)

Observed Wave Number	Calculated Wave Number		Potential Energy Distribution
	$\text{H}^{\text{S}}\text{H} \text{H}^{\text{S}}\text{H} \text{C}^{\text{S}}\text{H}$ (TTTG)	$\text{H}^{\text{S}}\text{H} \text{H}^{\text{S}}\text{C} \text{H}^{\text{S}}\text{H}$ (TTG'T)	
525m	518		$\text{ccc}_1(20), \text{x}_3(18), \text{x}_{\pi 2}(15)$
	607		$\text{x}_1(44), \text{x}_2(27)$
610s		611	$\text{x}_1(53), \text{x}_3(16)$
620		616	$\text{x}_3(55), \text{x}_1(17)$
628sh	626		$\text{x}_2(43), \text{x}_1(27)$
688s	680		$\text{x}_3(54), \text{w}_{13}(11)$
		689	$\text{x}_2(54), \text{w}_{12}(11)$
810w			
850m	850		$\text{r}_2(33), \text{r}_1(28)$
		855	$\text{r}_2(40)$
		886	$\text{r}_1(41), \text{B}_{21}(13)$
881m	888		$\text{R}_6(16), \text{R}_6(12)$
		910	$\text{B}_{12}(22), \text{R}_5(16)$
910msh			
917m	916		$\text{B}_{22}(14), \text{B}_{12}(13), \text{r}_2(12)$
	923		$\text{R}_2(18), \text{r}_2(17), \text{B}_{11}(15)$
		931	$\text{R}_2(16), \text{B}_{11}(16)$
		975	$\text{B}_{22}(28), \text{R}_3(13)$
967s			
984s	993		$\text{B}_{21}(26), \text{B}_{22}(13)$
		1005	$\text{B}_{21}(29), \text{B}_{22}(12)$
1009m	1012		$\text{B}_{22}(29), \text{B}_{12}(18)$
	1030		$\text{R}_4(23), \text{t}_2(11)$
1054m		1059	$\text{R}_3(12)$
1072m		1069	$\text{R}_6(21), \text{R}_4(15), \text{R}_1(15)$
1083vw	1081		$\text{R}_1(27), \text{R}_6(12)$
	1090		$\text{R}_3(33)$
1090vw		1094	$\text{R}_1(26), \text{R}_6(17)$
1106w	1105		$\text{R}_4(20), \text{R}_1(14), \text{t}_1(14)$
		1117	$\text{R}_4(20), \text{R}_2(12), \text{R}_6(11)$
1122s		1120	$\text{t}_2(20)$
	1131		$\text{R}_3(16), \text{R}_2(15)$
	1136		$\text{R}_5(21), \text{R}_2(13)$
		1140	$\text{R}_3(17), \text{R}_2(11)$
1167vwsh		1164	$\text{R}_5(15), \text{t}_2(14), \text{t}_1(11)$
1183m	1179		$\text{t}_1(27), \text{H}_{\sigma 2}(12)$
	1196		$\text{t}_2(31), \text{H}_{\sigma 2}(13)$
1204m			

Table V--(concluded)

Observed Wave Number	Calculated Wave Number		Potential Energy Distribution
	$\text{H}^{\text{S}}\text{H} \text{H}^{\text{S}}\text{H} \text{C}^{\text{S}}\text{H}$ (TTTG)	$\text{H}^{\text{S}}\text{H} \text{H}^{\text{S}}\text{C} \text{H}^{\text{S}}\text{H}$ (TTG'T)	
		1197	$\text{H}_{\sigma 2}(18), t_2(14), \text{H}_{\sigma 3}(12), t_1(11)$
1230msh	2x528 = 1256 2x610 = 1220		
1245s	1246		$\text{H}_{\sigma 3}(71)$
1255msh	1261	1251	$\text{H}_{\sigma 2}(40), \text{H}_{\sigma 1}(35)$
			$w_1(21), \text{H}_{\pi 2}(20), w_2(17)$
1273s	1263	1263	$\text{H}_{\sigma 3}(48), \text{H}_{\pi 2}(11)$
			$\text{H}_{\sigma 1}(51), \text{H}_{\sigma 2}(16)$
1287m	1290	1282	$\text{H}_{\sigma 1}(19), \text{H}_{\pi 1}(13), t_1(11)$
			$\text{H}_{\sigma 2}(23), \text{H}_{\pi 1}(14)$
		1290	$\text{H}_{\pi 3}(19), w_1(15), w_2(13)$
		1303	$t_1(21), w_2(12)$
1314m	1314		$t_1(24), \text{H}_{\pi 1}(23)$
1322m		1329	$\text{H}_{\pi 1}(16), \text{H}_{\pi 2}(15), t_2(15)$
			$t_2(22), \text{H}_{\pi 3}(21)$
1348vw	1332		$w_1(14), w_2(13), u_1(11)$
1358w	1363	1356	$u_1(19), w_1(16), u_2(15)$
			$u_2(32), u_1(17), \text{H}_{\pi 2}(11)$
1383s	1371	1373	$u_2(29), u_1(24)$
		1388	$u_1(35), u_2(28)$
		1391	$u_1(37), u_2(13), w_1(11)$
		1395	$u_2(22), w_2(14)$
		1397	$u_2(14), w_2(11)$
1423	1425		$\delta_1(67), \delta_2(25)$
		1426	$\delta_1(83)$
1438wsh	1430		$\delta_2(64), \delta_1(26)$
		1431	$\delta_2(75)$
1448s	1459		$A_{11}(45), A_{21}(25), A_{12}(14)$
		1459	$A_{11}(40), A_{21}(28), A_{12}(13)$
			$A_{21}(48), A_{11}(24), A_{22}(11)$
		1459	$A_{21}(45), A_{11}(29)$
1458msh	1459		$A_{12}(71), A_{11}(19)$
		1459	$A_{22}(71), A_{21}(14)$
		1459	$A_{12}(66), A_{11}(19)$
		1460	$A_{22}(75), A_{21}(15)$

^aReferences 6 and 11.

^bSee Reference 2 for definitions of coordinates.

664 cm^{-1} and 699 cm^{-1} for the $\text{H}^{\text{S}}\text{H}_2\text{C}^{\text{S}}\text{H}_2\text{C}^{\text{S}}\text{H}_2$ conformer, and at 666 cm^{-1} and 689 cm^{-1} for the $\text{H}^{\text{S}}\text{C}^{\text{H}}\text{H}_2\text{C}^{\text{S}}\text{H}_2$ form. The higher frequency in each conformer is assigned to the strong observed band at 688 cm^{-1} . Since no bands were observed close to 666 cm^{-1} the other two calculated frequencies are left unassigned. The two observed bands at 563

cm^{-1} and 635 cm^{-1} , and the identification of the ${}_{\text{H}}\text{S}_{\text{HH}}\text{S}_{\text{H}}$ and ${}_{\text{H}}\text{S}_{\text{HH}}\text{S}_{\text{H}}$ conformers in isotactic 2,4-dichloropentane, encouraged us to calculate the vibrational frequencies for the ${}_{\text{H}}\text{S}_{\text{HH}}\text{S}_{\text{HH}}\text{S}_{\text{H}}$ and ${}_{\text{H}}\text{S}_{\text{HH}}\text{S}_{\text{HH}}\text{S}_{\text{H}}$ conformations of isotactic 2,4,6-trichloroheptane. As seen from Table IV, the ${}_{\text{H}}\text{S}_{\text{HH}}\text{S}_{\text{HH}}\text{S}_{\text{H}}$ conformer has predicted bands at 565 cm^{-1} and 628 cm^{-1} , in reasonable agreement with the observed bands at 563 cm^{-1} and 635 cm^{-1} . We think it likely that this conformer is present at room temperature. A calculated band at 568 cm^{-1} for the ${}_{\text{H}}\text{S}_{\text{HH}}\text{S}_{\text{HH}}\text{S}_{\text{H}}$ conformer may also be consistent with the presence of some of this isomer.

The assignment of the observed C-Cl stretching vibrations in the heterotactic stereoisomer is not complicated. Two rotational isomers are predicted to be present, ${}_{\text{H}}\text{S}_{\text{HH}}\text{S}_{\text{HC}}\text{S}_{\text{H}}$ and ${}_{\text{H}}\text{S}_{\text{HH}}\text{S}_{\text{CH}}\text{S}_{\text{H}}$. In the first conformer there are two adjacent syndiotactic ${}_{\text{H}}\text{S}_{\text{H}}$ C-Cl stretching modes which interact and split, and one ${}_{\text{C}}\text{S}_{\text{H}}$ mode associated with the isotactically placed chlorine atom. The observed bands at 610 cm^{-1} , 628 cm^{-1} , and 688 cm^{-1} are assigned to the predicted bands at 607 cm^{-1} , 626 cm^{-1} , and 680 cm^{-1} , respectively. In the ${}_{\text{H}}\text{S}_{\text{HH}}\text{S}_{\text{CH}}\text{S}_{\text{H}}$ conformer the two ${}_{\text{H}}\text{S}_{\text{H}}$ modes are not adjacent and do not interact to produce appreciable splitting. These vibrations, calculated at 611 cm^{-1} and 616 cm^{-1} , are assigned to observed bands at 610 cm^{-1} and 620 cm^{-1} . The ${}_{\text{H}}\text{S}_{\text{C}}$ vibration which is predicted at 689 cm^{-1} is assigned to the observed band at 688 cm^{-1} . The observed spectra in the region from 425 cm^{-1} to 600 cm^{-1} are also well accounted for in terms of these two conformations of the heterotactic isomer. Higher frequency vibrations agree well with predicted frequencies, but are found to be less sensitive to conformation than are the vibrations which occur below 700 cm^{-1} .

DISCUSSION

The results of normal coordinate calculations of the vibrational modes of 2,4-dichloropentane and 2,4,6-trichloroheptane are reported. The validity of the general valence force field for secondary chlorides used in these calculations (δ) is supported by the good agreement obtained between observed and predicted bands.

In order to account for several weak infrared and Raman bands in the spectra of *dl*- and *meso*-2,4-dichloropentane and of 2,4,6-trichloroheptane, it is necessary to relax the restrictions to preferred conformations which are dictated by energy calculations on staggered, tetrahedral molecular models. According to Sykora (5), who has searched the continuum of molecular conformations (using a nonstaggered model) for local energy minima, the staggered model is a good approximation for the preferred conformation but fails to predict accurately the relative importance of the higher energy structures. Flory and Williams (12) evaluated statistical weight parameters, from which the conformer populations of the stereoisomers of 2,4-dichloropentane and 2,4,6-trichloroheptane were determined. Their results also indicate that previously ignored rotational isomers are present in some abundance at room temperature.

Attempts to interpret the NMR spectra of 2,4-dichloropentane have most often been made in terms of the presence of only the preferred structures. However, Schneider *et al.* (4) report that the NMR spectra of *dl*-2,4-dichloropentane cannot be adequately explained in terms of the structures predicted by the staggered molecular model. The temperature dependence of the vicinal coupling constants in the *meso* stereoisomer also suggest the presence of more than one isomer (4).

Evidence is presented here which strongly indicates that at room temperature the *dl* isomer of 2,4-dichloropentane contains, in addition to the ${}_H S_{HH} S_H$ and ${}_H S_{CC} S_H$ forms, measurable amounts of the ${}_H S_{HH} S_H$, ${}_H S_{HC} S_H$, and ${}_H S_{CH} S_H$ conformations. Meso-2,4-dichloropentane exists in the preferred ${}_H S_{HC} S_H$ form as well as in the ${}_H S_{HH} S_H$ and ${}_H S_{HH} S_H$ conformations. Likewise, the interpretation of the spectra of the stereoisomers of 2,4,6-trichloroheptane require the admission of conformations which were previously believed to be sterically disfavored. In particular, in the C-Cl stretching region isotactic 2,4,6-trichloroheptane contains absorption bands which can only be interpreted in terms of less favored structures.

Because the force field refined for secondary chlorides (8) gives such good agreement with the observed vibrational spectra, we feel that the present results provide compelling evidence for the existence of conformers other than the most preferred. Since many of these had previously been rejected on the basis of steric considerations, it is clear that a more realistic analysis of their exact structures [probably along the lines proposed by Sykora (5)] is necessary.

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