

Vibrational analysis of 2,3-dichlorobutanes

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Abstract—Using intensity changes from liquid to solid for *meso*- and *racemic*-2,3-dichlorobutanes, and preliminary normal mode calculations based on a force field for secondary chlorides, we have been able to identify the bands associated with the *trans* and *gauche* conformers of these molecules and thereby to refine a force field for secondary Cl atoms on vicinal C atoms. This has permitted assignment of the S_{HCl} , as well as S_{HH} and $S_{\text{HH'}}$, C-Cl stretch modes in such molecules.

INTRODUCTION

The vibrational analysis of small halogenated hydrocarbons can be important not only in studying their conformational structures but also in providing a basis for interpreting the spectra of polymers for which they serve as models. Thus, an analysis of secondary chlorides [1, 2] resulted in a force field that could be tested on 2,4-dichloropentanes [2, 3] and 2,4,6-trichloroheptanes [3], and was subsequently used to analyze the spectrum of crystalline syndiotactic poly(vinyl chloride) [4]. Although empirical studies had led to the characterization of nonplanar zigzag syndiotactic as well as isotactic poly(vinyl chloride) chain conformations [5], the above results of vibrational analysis now allow definitive assignments to be made to rotational isomeric states of this polymer as a function of polymerization conditions [6, 7] and physical state [8, 9].

A comparable vibrational analysis of 2,3-dichlorobutanes would provide a similar basis for studying conformational structures in polymers such as chlorinated polyethylenes and addition-chlorinated polyalkenes. And an extension of such an analysis to 2,3,4-trichloropentanes would allow the characterization of conformations in chlorinated poly(vinyl chloride). In addition, empirical studies of 2,3-dichlorobutanes have led to contradictory assignments of spectral bands to conformational states [10-12]. We have therefore undertaken a force field refinement for this molecule, the results of which are presented here. The application of this force field to the analysis of conformation in chlorinated poly(butadiene)s is given elsewhere [13].

The carbon-chlorine stretching frequencies in secondary chlorides have been shown to be sensitive to the conformation of the molecule in the vicinity of the C-Cl bond [5, 14]. For the *meso* and *racemic* forms of 2,3-dichlorobutane these conformational states are related to the *trans* or *gauche* rotation about the central C-C bond. In this work we have chosen to designate each conformation by a notation that gives both of the above characteristics as well as the

configuration of the molecule. This is shown in Fig. 1, where the symbols have the following meanings: M represents a methyl carbon; R and S represent the type of asymmetric carbon (in this convention if the carbon atom is in the plane of the paper and the hydrogen atom is below, then R corresponds to a clockwise, and S to a counterclockwise, sequence of Cl, CHCICH₃ and CH₃); T, G, and G' are the usual designations for *trans* and *gauche* forms of the carbon backbone; and S_{XY} refers to a secondary chloride with X and Y atoms trans to the Cl atom across the two adjacent C-C bonds (S_{HH} signifies that the carbon backbone is not planar zigzag [5]). The *trans* conformer of the *meso* form (MRSM-T/ S_{HCl}) has an inversion center, while the *gauche* conformers (MRSM-G/ S_{HH} S_{HC} and MRSM-G'/ S_{HH} S_{HC}) have no symmetry but are mirror images of each other. Each of the three conformers of the *racemic* form (MRRM or MSSM) has a two-fold rotation axis.

EXPERIMENTAL

The stereoisomers of 2,3-dichlorobutane were provided to us by the B. F. Goodrich Co. Infrared and Raman spectra showed that their purity was sufficient for our purposes.

Infrared spectra between 3100 and 400 cm⁻¹ were obtained on a Perkin-Elmer 180 spectrophotometer, at a spectral resolution of 2.0 cm⁻¹. Both room and liquid nitrogen temperature spectra were recorded. Between 400 and 80 cm⁻¹ a Digilab FTS-14 FTIR instrument was used. Sample thicknesses were about 0.5 mm, and at room temperature 160 scans were taken, with a spectral resolution of 1.0 cm⁻¹, while at liquid nitrogen temperature 1000 scans were taken, with a spectral resolution of 4.0 cm⁻¹.

Raman spectra were obtained on an instrument built in this laboratory [15]. Samples in capillaries were studied, at room and at liquid nitrogen temperatures, with 5145 Å exciting light at a power of 100 mW. Data were accumulated for 0.3 s at each sampled frequency, with 2-16 scans being taken depending on the signal-to-noise ratio. Spectral resolution was about 1 cm⁻¹.

NORMAL VIBRATION CALCULATION

The structural parameters used in the calculations were: $r(\text{CH}) = 1.09 \text{ \AA}$, $r(\text{CC}) = 1.54 \text{ \AA}$, $r(\text{CCl}) = 1.79 \text{ \AA}$;

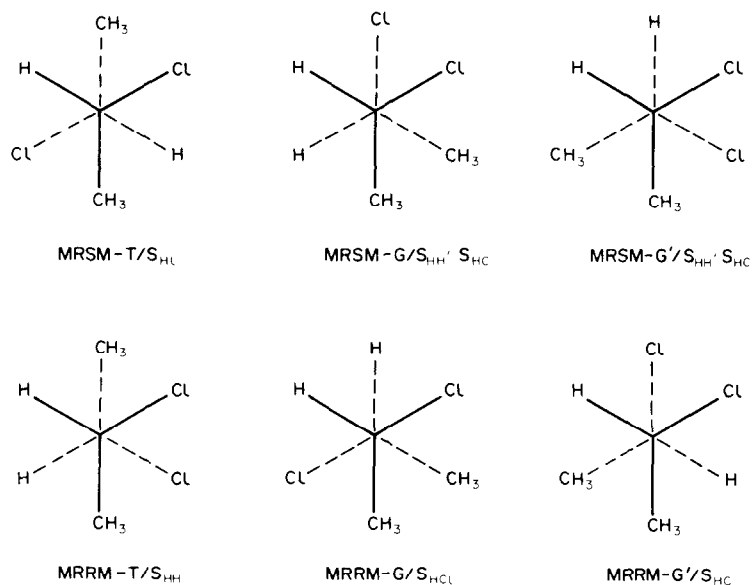


Fig. 1. Designation of conformations of *meso* (MRSM) and *racemic* (MRRM) 2,3-dichlorobutanes (see text for description of symbols).

all bond angles were assumed to be tetrahedral, and dihedral angles were taken to be 180° and $\pm 60^\circ$ for *trans* and *gauche* conformations, respectively. Although some of these values are variable in the literature, we think that the above choices are reasonable ones. The actual *gauche* dihedral angles may be

slightly different from the above standard values [2], but we think the latter are close enough to permit a reliable analysis of rotational isomeric states.

Local symmetry coordinates were used in the calculations, and their definitions are given in Table 1. The torsion coordinate was defined as the average of the

Table 1. Local symmetry coordinates for 2, 3-dichlorobutanes

Group	Name	Symbol	Definition
CH ₃	Symmetric stretch	M ss	$1/\sqrt{3} (\text{CH}^1 + \text{CH}^2 + \text{CH}^3)^a$
	Antisymmetric stretch 1	M as1	$1/2 (2\text{CH}^1 - \text{CH}^2 - \text{CH}^3)$
	Antisymmetric stretch 2	M as2	$1/\sqrt{2} (\text{CH}^2 - \text{CH}^3)$
	Symmetric bend	M sb	$1/\sqrt{6} (\text{H}^2\text{CH}^3 + \text{H}^1\text{CH}^3 + \text{H}^1\text{CH}^2 - \text{CCH}^1 - \text{CCH}^2 - \text{CCH}^3)$
	Antisymmetric bend 1	M ab1	$1/2 (2\text{H}^2\text{CH}^3 - \text{H}^1\text{CH}^3 - \text{H}^1\text{CH}^2)$
	Antisymmetric bend 2	M ab2	$1/\sqrt{2} (\text{H}^1\text{CH}^3 - \text{H}^1\text{CH}^2)$
	Rock 1	M r1	$1/2 (2\text{CCH}^1 - \text{CCH}^2 - \text{CCH}^3)$
	Rock 2	M r2	$1/\sqrt{2} (\text{CCH}^2 - \text{CCH}^3)$
CHCl	CH stretch	CH s	
	CCl stretch	CX s	
	CH parallel bend ^b	CH b _π	$1/\sqrt{2} (\text{MCH} - \text{CCH})^c$
	CH perpendicular bend ^b	CH b _σ	$1/2 (2\text{HCX} - \text{MCH} - \text{CCH})$
	CCl parallel bend	CX b _π	$1/\sqrt{2} (\text{MCX} - \text{CCX})$
	CCl perpendicular bend	CX b _σ	$1/\sqrt{6} (\text{MCX} + \text{CCX} - \text{MCC} - \text{HCM} - \text{HCC} - \text{HCX})$
	Backbone deformation	C d	$1/2 (2\text{MCC} - \text{MCX} - \text{CCX})$
CH ₃ -CHCl	MC stretch	MC s	
	MC torsion	MC t	
CHCl-CHCl	CC stretch	CC s	
	CC torsion	CC t	

^aCH¹ is the bond *trans* to the non-methyl C-C bond.

^bParallel and perpendicular are defined with respect to the C(H₃)-C(HCl)-C(HCl) plane.

^cM is the carbon atom of the CH₃ group.

torsional displacements over all possible dihedral angles around a single bond. In order to take advantage of the center of symmetry in MRSM-T, we constructed a set of molecular symmetry coordinates for this molecule from the local symmetry coordinates. This permitted the factoring of the G , F and GF matrices into two blocks, corresponding to Raman-active (A_g) and i.r.-active (A_u) species.

The starting force field was that refined for secondary chlorides by MOORE and KRIMM [2] (referred to as M-K hereafter). Since this force field did not deal with structures having Cl atoms on adjacent C atoms, for our initial calculations we estimated the necessary new force constants by transferring from the M-K force field those that involved similar internal coordinates

and setting equal to zero those not in the M-K list. Our force field includes all interaction constants between two bond angles that have a bond in common, but does not include those between two angles that have only an apex atom in common or that have neither a bond nor an apex atom in common. We still consider interactions such as those between CCl stretch and C'CC" bend, and between C'C stretch and HCC" bend, namely in which there is one atom shared by a bond and an angle. Such a set of force constants gives quite good agreement between observed and calculated frequencies for both MRSM and MRRM.

On the basis of a calculation with the starting force field, and using the temperature variation of the band intensities, we were able to assign the observed bands

Table 2. Force constants for 2, 3-dichlorobutanes

Constant ^{a,b}	Value ^c		Constant ^{a,b}	Value ^c	
	Present	MK		Present	MK
1. f(MH)	4.7522	4.6990	34. f(HMH,CMH)	0.0040	0.0
2. f(CH)	4.6932	4.8460	35. f(CMH,CMH)	-0.0284	-0.0272
3. f(MC)	4.7047	4.7047	36. f(MCH,HCX)	0.1360	0.1055
4. f(CC)	4.7264	4.7047	37. f(MCH,CCH)	0.0236	0.0210
5. f(CX)	2.7844	2.7844	38. f(MCH,MCX)	0.0999	0.0
6. f(HMH)	0.5390	0.5390	39. f(CCH,HCX)	0.1120	0.1055
7. f(CMH)	0.6182	0.6213	40. f(CCH,CCX)	-0.2457	0.0
8. f(MCH)	0.6747	0.6567	41. f(MCX,HCX)	-0.0551	0.0
9. f(CCH)	0.5807	0.6567	42. f(MCX,CCX)	-0.0324	0.0
10. f(MCX)	1.1062	1.1062	43. f(CCX,HCX)	-0.0646	0.0
11. f(CCX)	1.2993	1.1062	44. f(MCC,MCH)	-0.0868	-0.0903
12. f(HCX)	0.8631	0.8518	45. f(MCC,CCH)	-0.1753	-0.0903
13. f(MCC)	1.0907	0.9792	46. f(MCC,MCX)	-0.0149	0.0
14. f(MCt)	0.1460	0.1309	47. f(MCC,CCX)	-0.2340	0.0
15. f(CCt)	0.3105	0.1309	48. f(HMC,MCH) _T	0.0830	0.0830
16. f(MH,MH)	0.0010	0.0190	49. f(HMC,MCH) _G	-0.0180	-0.0327
17. f(MC,CC)	0.2691	0.4058	50. f(HMC,MCX) _T	-0.1560	-0.1548
18. f(MC,CX)	0.6401	0.6401	51. f(HMC,MCX) _G	-0.1013	-0.1085
19. f(CC,CX)	0.3959	0.6401	52. f(HCC,CCH) _T	0.0807	0.0807
20. f(CM,CMH)	0.1845	0.1845	53. f(HCC,CCH) _G	-0.0855	-0.0327
21. f(MC,MCH)	0.1701	0.1701	54. f(HCC,CCX) _T	-0.0633	-0.1548
22. f(MC,MCX)	0.1003	0.1003	55. f(HCC,CCX) _G	-0.2978	-0.1085
23. f(MC,MCC)	0.3584	0.3490	56. f(XCC,CCX) _T	-0.1798	0.0
24. f(CC,CCH)	-0.0262	0.1701	57. f(XCC,CCX) _G	0.1309	0.0
25. f(CC,CX)	0.2322	0.1003	58. f(CCM,CMH) _T	0.0157	0.0730
26. f(CC,MCC)	0.3744	0.3490	59. f(CCM,CMH) _G	-0.0664	-0.0640
27. f(CX,HCX)	0.2399	0.2399	60. f(MCC,CCH) _T	-0.0903	0.0730
28. f(CX,MCX)	0.4005	0.4005	61. f(MCC,CCH) _G	-0.1183	-0.0077
29. f(CX,CCX)	0.5617	0.4005	62. f(MCC,CCX) _T	-0.1218	-0.0774
30. f(CX,MCC)	-0.0588	-0.1117	63. f(MCC,CCX) _G	0.0754	-0.0193
31. f(MC,HCC)	-0.1153	-0.0868	64. f(MCC,CCM) _T	-0.0933	0.0950
32. f(CC,HCM)	-0.1117	-0.0868	65. f(MCC,CCM) _G	-0.1302	0.0436
33. f(HMH,HMH)	0.0091	0.0	66. f(MCt,CCt)	0.0080	0.0080

^aM is the carbon atom of a CH₃ group, C is the carbon atom of a CHCl group, X is the Cl atom; t, torsion; in $f(XCC, CCY)_{T(G)}$ atoms X and Y are *trans(gauche)* to each other.

^bFor the stretch-stretch constants (16-19) one atom is shared in common; for the stretch-bend constants one bond is common (20-29) or one atom is common (30-32); for the bend-bend constants one bond and one apex atom are common (33-47) or one bond only (but no apex atom) is common (48-65).

^cStretch and stretch, stretch force constants are in mdyn/Å, while stretch, bend and bend force constants are in mdyn.

of MRSM and MRRM to the MRSM-*T*, MRSM-*G*, MRRM-*T* and MRRM-*G* conformers. We then used these assignments to refine the force constants associated with the CHCICHCl structure (all other non-zero force constants in the M-K force field were kept constant in the refinement, except for CH stretch, HCCl bend, and CH₃-CHCl torsion, which were refined to give better agreement with CH stretch, CH bend and torsion modes). The frequencies used in the refinement were those observed in only the i.r. or Raman spectra, or if they appeared in both their relative intensity-weighted average was used. The M-K and our final refined force fields are given in Table 2. For the four structures used in the refinement the average difference between observed and calculated frequencies is less than 4.7 cm⁻¹.

RESULTS AND DISCUSSION

Meso-2,3-dichlorobutanes

As mentioned earlier, *meso*-2,3-dichlorobutane has three rotational isomers: MRSM-*T*, which has a center

of symmetry, and to which therefore the mutual exclusion rule should apply; and MRSM-*G* and MRSM-*G'*, which have no symmetry but are mirror images of each other. These characteristics are helpful in assigning conformational structures in the liquid and solid states, and it has already been noted [11, 12] that both conformers coexist in the liquid whereas only the MRSM-*T* form is present in the solid state.

Our i.r. and Raman spectra show that (a) about half of the bands disappear on solidifying the sample, these bands not in general obeying the mutual exclusion rule, and (b) the bands that remain in the solid state do obey the mutual exclusion rule. This provides strong, and in fact unique, evidence that the solid sample is composed entirely of the *trans* conformer whereas in the liquid an equilibrium mixture of *trans* and *gauche* conformers is present. A clear separation is possible, therefore, of bands associated with each conformer, and this assignment is given in Table 3. It is interesting to note that many very weak bands in the solid state spectra can be assigned to combinations of fundamental frequencies of the *trans* conformer.

The above assignments, when combined with pre-

Table 3. Observed i.r. and Raman bands (in cm⁻¹) of *meso*-2,3-dichlorobutane

Infrared		Raman		Conf ^a	Infrared		Raman		Conf ^a
Liq.	Solid	Liq.	Solid		Liq.	Solid	Liq.	Solid	
2995sh	2996sh	2991w	3001s	T G			1122mw	1120w	T _g
2986vs	2989vs		2988mw	T G	1084w		1090ms		G
	2968mw	2968vw	2950w	?	1073m	1073s			T _u
2935s	2935m	2938vs	2940vs	T G	1057s		1061vw		G
2874mw	2867mw	2874mw	2870w	T G		1056vw			c
2825vw	2815vw			c	1048sh		1052mw		G
2740vw	2730vw			c		1032vw			c
2635vw	2633vw			c			1019ms	1016m	T _g
	1491vw			c	1007s	1003vs			T _u
1457sh	1462s	1454s	1461m	T G	980w		981vw		G
1443vs	1438s	1447sh	1448m	T G	967s	967vs	967ms		T _u G
			1437vw	c		931vw			c
	1418vw			c	849ms		846vs	848s	T _g G
	1393vw			c	697s		703vs	694vs	T _g G
1379vs	1378s	1385w	1383w	T G	652vs	643vs	650s		T _u G
		1357mw	1358mw	T _g	531m		533mw		G
	1354vw			c			483m	483s	T _g
1328m		1332w		G	419s		421m		G
1309w		1313vw		G	358s	359s			T _u
1289w	1288mw			T _u	349sh		344m	343m	T _g G
	1258vw			c	335m	339s			T _u
1252m		1252s	1253m	T _g G	301w		303vw		G
1235ms		1237w		G	280sh		280m	286s	T _g G
	1202sh			c	262m	255m	262vw		T _u G
1199s	1194vs			T _u	230vw		231vw	233vw	T _g G
	1180vw			c	210m	217s			T _u
		1162m	1163m	T _g			187w		G
1149mw		1152w		G	88s	121s	98w	90w	T _u G

^aT, *trans*; G, *gauche* conformer. c, combination band, which can be accounted for by fundamentals of the *T* conformer: 846(*g*) + 652(*u*) = 1498(*u*); 1162(*g*) + 280(*g*) = 1442(*g*); 344(*g*) + 1073(*u*) = 1417(*u*); 1122(*g*) + 262(*u*) = 1384(*u*); 703(*g*) + 652(*u*) = 1355(*u*); 1162(*g*) + 88(*u*) = 1250(*u*); 1122(*g*) + 88(*u*) = 1210(*u*); 846(*g*) + 335(*u*) = 1181(*u*); 846(*g*) + 210(*u*) = 1056(*u*); 703(*g*) + 335(*u*) = 1038(*u*); 280(*g*) + 652(*u*) = 932(*u*).

liminary normal mode calculations based on the M-K force field, permitted us to correlate observed bands with specific normal modes, and thus to refine the force constants. The major change that we made was in the CH stretch region, where the M-K force field predicts higher frequencies for C(Cl)-H stretch than for CH₃ stretch. The room temperature i.r. spectrum shows four medium to very strong bands in the CH stretch region, with the very strong band near 2990 cm⁻¹ being clearly composed of two peaks. Since addition-chlorinated polybutadiene has no absorption above 2960 cm⁻¹ [13], we assign the above peaks to CH₃ antisymmetric stretch, leaving the bands at 2935 and 2874 cm⁻¹ to be assigned to C(Cl)-H stretch and CH₃ symmetric stretch, respectively. The force constants given in Table 2 were refined on this basis, and are consistent with results on *n*-paraffins [16].

A detailed comparison between observed bands and

calculated frequencies obtained from the final refined force field is given in Tables 4 and 5 for MRSM-*T* and MRSM-*G*, respectively. In the latter case over a dozen bands are observed in frequency regions where overlap does not occur with modes of MRSM-*T*, and thus these bands serve as unique identifiers of the MRSM-*G* conformer. Of particular interest, as we will discuss below, is that CCl stretch contributes to bands near 650 and 700 cm⁻¹ for both MRSM-*T* and MRSM-*G*, as expected for secondary chlorides [2, 5], but also to bands in the lower frequency region, down to 340 cm⁻¹ for the former and 420 cm⁻¹ for the latter conformer. In most of these modes CCl stretch is strongly mixed with skeletal deformation. It is also noteworthy that the symmetry of MRSM-*T* permits the separation of MC torsion from CC torsion, the former appearing in the 260-280 cm⁻¹ region and the latter near 100 cm⁻¹.

Table 4. Observed and calculated frequencies (in cm⁻¹) of MRSM-*T* 2,3-dichlorobutane

Observed		Calculated		Potential Energy Distribution ^a
Raman	Infrared	A _g	A _u	
		2991		M as1(86), M as2(13)
		2990		M as2(87), M as1(13)
	2995		2991	M as1(93)
	2986		2990	M as2(93)
2938		2941		CH s(98)
	2935		2932	CH s(99)
2874		2874		M ss(100)
	2874		2874	M ss(100)
1454		1454		M ab1(73), M ab2(14)
1447		1450		M ab2(78), M ab1(14)
	1457		1450	M ab2(70), M ab1(23)
	1443		1448	M ab1(70), M ab2(22)
1385		1387		M sb(64), CH bπ(16)
	1379		1383	M sb(92), MC s(15)
1357		1360		CH bπ(38), M sb(33), MC s(17), CC s(14)
	1289		1295	CH bσ(40), CH bπ(32)
1252		1257		CH bσ(69), MC s(14), CH bπ(11)
	1199		1202	CH bσ(47), CH bπ(36)
1162		1164		CC s(43), M r1(20), CH bπ(13), CX bσ(10)
1122		1113		MC s(43), M r1(17), M r2(10)
	1073		1073	MC s(51), M r2(23)
1019		1026		M r2(61), M r1(11)
	1007		1008	M r1(41), MC s(29), M r2(17)
	967		969	M r2(43), M r1(27), CH bπ(24)
846		847		CC s(41), M r1(38), MC s(18)
703		700		CX s(54), CX bσ(29), C d(24), CH bπ(21), M r2(15)
	652		658	CX s(100)
483		489		CX bσ(49), C d(17), MC s(12)
	358		365	CX bπ(54), C d(36), CX bσ(11)
344		343		CX s(39), C d(34)
	335		330	CX bσ(76), MC t(16), CX bπ(14)
280		278		MC t(95)
	262		269	MC t(77), CX bσ(18)
231		229		CX bπ(91), C d(13), CH bσ(10)
	210		205	C d(62), CX bπ(23)
	88		100	CC t(93)

^aOnly contributions of 10% or greater are included.

Table 5. Observed and calculated frequencies (in cm^{-1}) of MRRM-G 2,3-dichlorobutane

Observed	Calculated	Potential Energy Distribution ^a
2995	2991	M as1(92)
2991	2990	M as1(88)
2991	2990	M as2(91)
2986	2990	M as2(90)
2938	2936	CH s(99)
2935	2935	CH s(99)
2874	2874	M ss(100)
2874	2874	M ss(100)
1457	1452	M ab1(79), M ab2(10)
1454	1451	M ab2(68), M ab1(22)
1447	1450	M ab2(88)
1443	1448	M ab1(75), M ab2(13)
1385	1381	M sb(93)
1379	1380	M sb(97)
1329*	1337	CH b(68)
1311*	1311	CH b(33), CH b(26), CC s(23), MC s(13)
1252	1250	CH b(60), CC s(16), CH b(11)
1235*	1234	CH b(80), CC s(11)
1150*	1146	MC s(26), CH b(14), M r1(12)
1090*	1096	MC s(32), M r2(30)
1057*	1060	M r2(35), M r1(24), CX b(10)
1052*	1034	M r1(49), M r2(15), MC s(11)
980*	988	M r2(44), M r1(26)
967	966	M r2(34), MC s(28), CH b(21)
847	846	CC s(43), MC s(25), M r1(25)
697	700	CX s(60), C d(34), CX b(10)
650*	653	CX s(54), CX b(41), C d(16)
532*	537	CX s(48), CX b(32)
420*	422	CX s(31), CX b(21), CX b(18)
344	346	CX b(63), C d(27)
302*	291	MC t(41), C d(24), CX b(22), CX b(12)
280	279	MC t(93)
262	267	MC t(56), CX b(23), C d(19)
231	236	C d(62), CX b(38)
187*	188	CX b(52), CX b(25)
98	96	CC t(91)

^aOnly contributions of 10% or greater are included.

*Observed bands uniquely assignable (as a result of disappearance on solidification) to MRRM-G conformer.

Racemic-2,3-dichlorobutanes

Each of the three rotational isomers of racemic-2,3-dichlorobutane has C_2 symmetry, and therefore every normal mode is both i.r. and Raman active. The number of observed bands decreases on solidifying the sample, and it is therefore reasonable to assume that one or more conformers present in the liquid state are absent in the solid. There has been disagreement, however, over which conformer persists in the solid: some authors [11] propose that MRRM-G is the stable form in the solid, while others [12] suggest that the solid contains a mixture of MRRM-T and MRRM-G'. Our analysis resolves this question without ambiguity.

The assignment of observed bands to conformers was carried out using a comparison of intensity change between liquid and solid as well as results of a normal mode calculation. The preliminary calculation using the M-K force field clearly showed that those bands whose intensities increased (or at least did not decrease) on crystallization were associated with the MRRM-T conformer. We therefore assigned these bands, most of which were strong, to this conformer and did an initial refinement of the force field to the

observed frequencies of MRRM-T, MRRM-G and MRRM-T. A normal mode calculation using this force field then showed that several strong bands in the liquid that disappeared on solidification could be uniquely assigned to MRRM-G, with some weaker bands being assignable to MRRM-G'. Since the former assignment was relatively clear, we added the MRRM-G structure to the refinement procedure, and this led to the final set of force constants given in Table 2. In Table 6 we give the observed frequencies and the results of our assignments. As in the case of MRRM, we also find here that many very weak bands in the solid state spectra can be assigned to combinations of fundamental frequencies of the *trans* conformer.

A detailed comparison between observed bands and calculated frequencies for MRRM-T, MRRM-G and MRRM-G' is given in Tables 7, 8, and 9, respectively. Although the MRRM-G' frequencies were not used in the refinement procedure, the average difference between observed and calculated frequencies for this conformer is less than 7 cm^{-1} , indicating an acceptably transferable force field. The major discrepancies occur in the CH bend and CCl stretch modes of the CHCl group. This could be due to the uncertain assignments of observed bands to this isomer, or to the fact that actual structures may differ somewhat from the assumed ones of tetrahedral bond angles and $\pm 60^\circ$ dihedral angles. This result would not be surprising in view of the known sensitivity of CCl stretch frequencies to torsion angles about adjacent C-C bonds [2].

CCl stretch modes

In a study of a series of secondary monochlorohydrocarbons it was shown [5] that the CCl stretch mode is sensitive to the local backbone conformation, with the following correlations being observed: S_{HH} 608–615, $S_{HH'}$ 627–637 and S_{HC} 655–674 cm^{-1} . Normal mode analyses of 2-chlorobutane [1, 2] verified these assignments, and showed in addition that CCl stretch makes significant contributions to lower frequencies for some of the conformers (522 cm^{-1} for $S_{HH'}$ and 374 cm^{-1} for S_{HC}). For 2,4-dichloropentanes [2, 3], in which interactions are possible between the two CCl stretch modes, the above ranges are extended somewhat (S_{HH} being found up to 627, $S_{HH'}$ up to 650 and S_{HC} up to 715 cm^{-1}). Clearly, while the restricted regions can apply to monochlorohydrocarbons [5], the situation can get more complex when interactions between two CCl stretch modes are possible.

When secondary Cl atoms occur on vicinal C atoms the possibility of interactions increases significantly, and these interactions are expected to be particularly sensitive to local backbone conformation. In such cases it is especially important to have normal mode analyses so that oversimplified conclusions are not drawn.

In Table 10 we give a detailed description of the CCl stretch modes in the 2,3-dichlorobutanes, including the

Table 6. Observed i.r. and Raman bands (in cm^{-1}) of *racemic*-2,3-dichlorobutane

Infrared		Raman		Conf ^a	Infrared		Raman		Conf ^a
Liq.	Solid	Liq.	Solid		Liq.	Solid	Liq.	Solid	
2994sh	2996vs	3000w	3001ms	T G G'	956vs		956mw		G G'
2987vs	2978vs	2980mw	2981m	T G G'	855s	852s	855ms	848s	T G G'
2937s	2930s	2943vs	2948s	T G G'			828vw		G
2873w	2865w	2877mw	2864w	T G G'	729sh	723m	731vw	731w	c
1455sh	1453sh	1450s	1460s	T G G'	706s	698vs			T
1447s	1438vs		1439vw	T G G'	694sh		694vs	701s	T G G'
	1383sh	1383ms	1385w	T G G'	650vs		654vw		G G'
1379vs	1378s	1379sh	1378m	T G G'	597ms	591ms	598ms	588vs	T G
1350vw		1344vw		G	557w	556w	560w	567w	c
1329w	1334m			T	519s	515vs	520w	518m	T
1303m	1304s	1308w	1303w	T G G'	485w	486w	485w	486mw	T
1255ms	1254vs	1255s	1245w	T G G'	435m		435w		G'
1227vs	1227m	1232m	1229m	T G		410w			c
1215sh		1218sh		G'	392w		392vw		G'
1172vw	1172vw	1167m		c G G'	370m		370ms		G
			1133w	c	354ms	354s		360w	T G'
1126m	1128m	1125ms	1122s	T	342ms		342vw		G
1113vs	1119m			c G	320w			315w	G'
	1100w			c	309w	306w	308w	306vw	T
	1084w	1081w		T			280vw		T G G'
1070sh	1073vw			c G'	264vw		264vw		T G G'
1052vs	1045vw	1055w		c G G'	230mw	227m	231vw	237w	T G G'
1017m	1016s	1021s	1018w	T G	208s				G
995s	993vs	1003mw	996w	T G G'	196sh		199w	204mw	T G'
977m	978mw	978m	978m	T	102m	112w	104w	112w	T G G'

^aT, *trans*; G, *gauche*; G', *gauche'* conformers. c, combination band in solid state spectra, which can be accounted for by fundamentals of *T* conformer: $2 \times 591 = 1182$; $852 + 280 = 1133$; $1016 + 112 = 1128$; $993 + 112 = 1105$; $591 + 515 = 1106$; $591 + 486 = 1077$; $698 + 354 = 1052$; $486 + 227 = 713$; $354 + 204 = 558$; $306 + 112 = 418$.

potential energy contribution of this coordinate and a rough indication of the motions in the two C-Cl bonds. We note that there are only three pure CCl stretch modes, the $652(\text{vs}, \text{i.r.}) \text{cm}^{-1}$ band of *MRS*M-*T*, the $597(\text{ms}, \text{R}, \text{i.r.}) \text{cm}^{-1}$ band of *MRR*M-*T* and the $650(\text{vs}, \text{i.r.}) \text{cm}^{-1}$ band of *MRR*M-*G*. The others are mixed with various deformation coordinates. Some regularities nevertheless emerge. The main S_{HH} frequency, 597cm^{-1} of *MRR*M-*T*, is found near the expected range, although the other S_{HH} mode of this conformer at $706(\text{s}, \text{i.r.}) \text{cm}^{-1}$, is far removed. The S_{HH} frequencies (of *MRS*M-*G*) are found near the expected range (including the low frequency), even though the CCl stretch contribution is not predominant. The higher S_{HC} frequencies of *MRS*M-*G* and *MRR*M-*G'* are within the range found in 2,4-dichloropentane, although the lower frequency of *MRR*M-*G'* ($\sim 650 \text{cm}^{-1}$) moves slightly below the typical lower limit. The S_{HCl} frequencies in *MRS*M-*T* and *MRR*M-*G*, are found near 650 and 700cm^{-1} , the former strong in the infrared and the latter strong in the Raman. These may serve to characterize S_{HCl} modes in linear chlorohydrocarbons having Cl atoms on vicinal C atoms. (It is interesting to note that in cyclohexanes with Cl atoms on vicinal C atoms the S_{HCl} frequencies are found at 610 and 690cm^{-1} [17].)

What emerges from these results is that the CCl stretch frequencies for vicinal CCl groups form a more complex pattern than when such groups are separated by a methylene group. Bands near 700cm^{-1} are contributed to by S_{HH} , S_{HC} and S_{HCl} conformations, bands near 650cm^{-1} are associated with S_{HH} , S_{HC} and S_{HCl} conformations, and only bands near 600cm^{-1} are uniquely associated with S_{HH} conformations. The various structures may still be assignable, however, by combined infrared and Raman studies in the CCl stretch region, as well as attention to characteristic frequency patterns in other regions.

CONCLUSIONS

By utilizing preliminary calculations based on a force field for secondary chlorides [2], and intensity changes that occur on solidification of the liquid, we have been able to make very confident assignments of i.r. and Raman bands to *trans* and *gauche* conformers of *meso*- and *racemic*-2, 3-dichlorobutanes. This has permitted us to refine a force field for hydrocarbon structures having Cl atoms on vicinal C atoms, with an average agreement of better than 5cm^{-1} between observed and calculated frequencies. When this force

Table 8. Observed and calculated frequencies (in cm^{-1}) of MRRM-G 2,3-dichlorobutane

Observed	Calculated	Potential Energy Distribution ^a
3000	2991	M as1(91)
2994	2991	M as1(92)
2987	2990	M as2(92)
2980	2990	M as2(91)
2943	2936	CH s(98)
2937	2935	CH s(99)
2877	2874	M ss(95)
2873	2874	M ss(99)
1455	1452	M ab1(68),M ab2(22)
1450	1450	M ab2(65),M ab1(17)
1450	1450	M ab2(69),M ab1(22)
1447	1448	M ab1(66),M ab2(26)
1383	1381	M sb(93),MC s(14)
1379	1380	M sb(96),MC s(10)
1347	1339	CH br(78),MC s(12)
1303	1295	CH bo(78)
1255	1257	CC s(54),CH br(34),M r1(14)
1227	1228	CH bo(92)
1167	1165	CH br(38),MC s(24),CC s(11)
1113	1121	MC s(34),M r1(24),CX bo(18),M r2(14)
1052	1041	M r2(72)
1021	1028	M r1(44),M r2(36)
995	988	M r1(56),MC s(22),CH br(20)
956	958	MC s(36),M r2(32),CH br(12)
831*	834	CC s(42),MC s(32),M r1(16)
694	703	CX s(56),C d(40),CH br(22),CX bo(18),M r2(14)
650	657	CX s(100)
597	593	CX bo(60),C d(20),M r1(14)
370*	369	CX s(36),CX bo(22),C d(20)
342*	343	CX br(76),C d(14)
280	285	MC t(74),CX br(12)
280	280	MC t(90)
264	254	CX br(34),CX bo(32),MC t(22),C d(20)
230	230	CX br(56),C d(36),CX bo(16)
208*	212	C d(48),CX bo(32),CX br(16)
102	99	CC t(93)

^aOnly contributions of 10% or greater are included.

*Observed bands uniquely assignable to MRRM-G conformer.

Table 7. Observed and calculated frequencies (in cm^{-1}) of MRRM-T 2,3-dichlorobutane

Observed	Calculated	Potential Energy Distribution ^a
3000	2991	M as1(94)
2994	2991	M as1(87),M as2(112)
2990	2990	M as2(87),M as1(112)
2980	2990	M as2(93)
2943	2936	CH s(99)
2937	2935	CH s(99)
2877	2874	M ss(100)
2873	2874	M ss(100)
1455	1452	M ab1(90)
1450	1450	M ab2(65),M ab1(27)
1450	1450	M ab2(92)
1447	1448	M ab1(66),M ab2(28)
1383	1383	M sb(92),MC s(14)
1379	1377	M sb(92)
1329	1326	CH br(49),CC s(24),MC s(24)
1303	1303	CH br(64),CH bo(18)
1255	1257	CH bo(70),CH br(12)
1255	1254	CH bo(68),CC s(27)
1227	1226	MC s(38),M r1(18),M r2(10),C d(10)
1084	1084	CH bo(24),M r1(24),CH bo(18),M r2(10)
1070	1072	MC s(40),M r2(40)
1017	1018	M r1(66),CH br(12)
995	1002	MC s(36),M r2(30),M r1(14)
978	977	M r2(65),CH br(24)
855	849	CC s(43),M r1(38),MC s(18)
706	698	CX s(52),CX bo(46),M r2(16),C d(12)
597	593	CX s(102),C d(14)
519	512	CX s(52),CX bo(26),CX br(12)
485	488	CX bo(32),C d(22),CX br(18),MC s(16)
354	352	C d(52),CX br(48)
309	297	C d(48),CX br(28),MC t(20),CX bo(14)
280	278	MC t(96)
264	271	MC t(76),C d(14),CX br(12)
230	225	CX br(38),C d(30),CX bo(24)
196	190	CX br(38),CX bo(38)
102	94	CC t(91)

^aOnly contributions of 10% or greater are included.

Table 9. Observed and calculated frequencies (in cm^{-1}) of MRRM-G' 2,3-dichlorobutane

Observed	Calculated	Potential Energy Distribution ^a
3000	2991	M as1(96)
2994	2991	M as1(81), M as2(18)
2987	2990	M as2(82), M as1(17)
2980	2990	M as2(95)
2943	2941	CH s(98)
2937	2932	CH s(100)
2877	2874	M ss(100)
2873	2874	M ss(100)
1455	1454	M ab1(78)
1450	1450	M ab2(76), M ab1(17)
1450	1450	M ab2(82)
1447	1448	M ab1(71), M ab2(16)
1383	1387	M sb(66), CH b π (14)
1379	1378	M sb(98), MC s(12)
1379	1373	CH b π (44), M sb(26), MC s(24), CC s(14)
1303(?)	1280	CH b σ (80)
1255	1270	CH b π (48), CH b σ (28), MC s(14)
1215*	1199	CH b σ (56), CH b π (28), M r1(12)
1167	1160	CC s(43), M r1(24)
-	1096	MC s(60), CH b σ (16)
1070	1075	MC s(36), M r2(28), CX b σ (10)
1052	1054	M r1(38)
995	1003	M r2(46), M r1(22), MC s(18)
956	957	M r2(46), CH b π (28), M r1(24)
855	863	CC s(41), M r1(34), MC s(20)
~700	714	CX s(66), C d(48), M r1(12)
~650	667	CX s(64), CX b σ (40), CH b π (14), M r2(12)
435*	442	CX b σ (38), CX s(34)
392*	390	CX b π (60), CX s(18), MC s(14)
354	363	CX b π (30), CX b σ (28), CX s(24), C d(18)
320*	321	CX b σ (66), C d(20), MC t(16)
280	279	MC t(92)
264	266	MC t(76), CX b σ (26)
264	249	C d(90), CX b π (36)
196	183	CX b π (66), C d(20)
102	99	CC t(90)

^aOnly contributions of 10% or greater are included.

*Observed bands uniquely assignable to MRRM-G' conformer.

field is transferred to the *gauche'* conformer of *racemic*-2, 3-dichlorobutane it gives a satisfactory prediction of bands that can be uniquely assigned to this conformer.

Our analysis clearly shows that the *trans* conformer of *racemic*-2, 3-dichlorobutane is the only stable form in the solid state, in contrast to previous conflicting predictions [11, 12]. Some weak bands in the solid state of both this molecule and *meso*-2, 3-dichlorobutane are readily assignable to combinations involving fundamentals of the *trans* conformer, and therefore they do not have to be ascribed to other conformers that may have normal mode frequencies near these values.

The simple correlations between CCl stretching frequency and backbone conformation found for secondary chlorides with either one CCl group [5], or more than one if they are separated by a CH₂ group [3], become more complex when vicinal C atoms are involved. This is undoubtedly due to the more significant coupling between the two CCl stretching modes that occurs in this case. We are, however, able to define the modes characteristic of the S_{HCl} species (see Table 10), and to specify the kinds of correlations that are likely for conformations involving vicinal CCl groups. It is clear that normal mode

Table 10. CCl stretch frequencies (in cm^{-1}) in 2,3-dichlorobutanes

Conformer	Cl Species	Frequencies	PED ^a	Eigenvector ^a	
				C ₂ -Cl	C ₃ -Cl
MRRM-T	S _{HCl}	703 (R)	54	+	+
		652 (IR)	100	+	-
		344 (R)	39	+	+
MRRM-G	S _{HH'} (C ₂)	650 (R) (IR?)	54	-	0
		532 (R, IR)	48	-	0
	S _{HC} (C ₃)	697 (IR) (R?)	60	0	-
		420 (R, IR)	31	0	+
MRRM-T	S _{HH}	706 (IR) (R?)	52	+	-
		597 (R, IR)	102	+	+
		519 (IR)	52	+	-
MRRM-G	S _{HCl}	694 (R)	56	+	+
		650 (IR)	100	-	+
		370 (R, IR)	36	+	+
MRRM-G'	S _{HC}	~700 (R, IR)	66	+	-
		~650 (R, IR)	64	-	-
		435 (R, IR)	34	-	-

^aComponent of potential energy distribution in CCl stretching.

^bDisplacements in C—Cl bonds: +, stretching; -, contraction.

analysis has been crucial in the present case in understanding the detailed nature of overlapping modes in the traditional 600–700 cm^{-1} CCl stretching region of secondary chlorides.

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