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Vibrational Analysis of 1,2-Dibromopropane and 1,2-Dibromopropane-D₆

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VIBRATIONAL ANALYSIS OF 1,2-DIBROMOPROPANE
AND 1,2-DIBROMOPROPANE-D₆

Keywords: Dibromopropane, Conformational analysis, Infrared spectra, Normal coordinate calculations

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ABSTRACT

Infrared spectra were obtained for 1,2-dibromopropane-d₆ in the liquid and in the unannealed and

annealed solid states. Vibrational assignments were made for the three conformers of 1,2-dibromopropane and the three conformers of 1,2-dibromopropane-d₆ with the aid of normal coordinate calculations. All three possible conformers of CD₂BrCDBrCD₃ were found to be present in the liquid and unannealed solid, but the P_HS_{HH} conformer was absent in the annealed solid.

INTRODUCTION

Vibrational spectra have been published for 1,2-dibromopropane, and this compound was shown by Thorbjornsrud, Ellestad, Klaboe, and Torgrimsen (TEKT) to exist as a mixture of three conformers in the liquid state.¹ A complete fundamental vibrational assignment was made for the conformer with the bromines in the anti (or trans) position. This conformer was present in much greater concentration in the neat liquid than was either of the other two conformers, and it was the only conformer present in the low-temperature crystalline solid.¹ Molecular mechanics calculations have been made for this compound that show the anti conformer to be the low-energy form by at least 1.6 kcal/mole.²

Since the vibrational assignment of the anti conformer was made by inspection, and assignments for the two gauche conformers were not made, normal coordinate calculations were made for all three conformers. In

addition, the deuterated compound is now available, so infrared spectra have been obtained for it, and normal coordinate calculations have been made for the three conformers of this compound.

EXPERIMENTAL

Infrared spectra were obtained with a Nicolet MX-1 FTIR spectrometer. The sample of CD₂BrCDBrCD₃ was obtained from Stohler/KOR and had a stated purity of 99%. There was no evidence of the presence of the protonated species, and the sample was used without further purification.

CALCULATIONS

Normal coordinate calculations were made with a Prime 9955 computer. The computer programs written by Schachtschneider^{3,4} were used for calculation of the G matrix (GMAT), for solution of the vibrational secular equation (VSEC), and for the least-squares refinement of selected force constants to fit the calculated to the observed frequencies (FPERT).

RESULTS AND DISCUSSION

1,2-Dibromopropane

Infrared and Raman spectra have been obtained for 1,2-dibromopropane by TEKT¹. This work included low-

temperature (-180°C) IR and Raman data and high-pressure (30 kbar) IR data. The low-temperature solid-state spectra showed the presence of only the A conformer (P_XS_{XH}), but there was a small amount of the G₊ conformer (P_CS_{HH}) present in the high-pressure solid.

Since all the low-temperature solid-state bands are due to the P_XS_{XH} conformer, normal coordinate calculations were first made for this conformer because there is no ambiguity in assignment of those bands to the correct conformer. A fifty-eight parameter modified valence force field was used that included fifteen diagonal and forty-three interaction force constants. The force constant values that had been obtained for 1,2-dichloropropane and 1,2-dichlorobutane⁵ were used, except for the C-Br stretching constant, which was taken from an alkyl bromide⁶ force field. The same value was used for the primary and secondary C-Br stretching constant, as has been done previously.^{6,7}

The initial calculated wavenumbers were not quite satisfactory, and several computer runs were made after manually adjusting several force constants. Wavenumbers were calculated for the other two conformers, then the FPERT program was used to adjust twenty force constants to fit the calculated to the observed wavenumbers for fifty-eight assigned values of the three conformers. The average difference between observed and calculated wavenumbers was 6.2 cm^{-1} .

Meyer and Ohmichi have done molecular mechanics calculations for 1,2-dibromopropane.² At 25°C, the concentration of the P_XS_{XH} conformer was calculated to be approximately 89%. This is for the vapor state, but the total amount of the two higher-energy forms is certainly greater than 11% in the neat liquid, as indicated by the presence of medium to strong liquid-state IR bands (1314, 1243, 1227, 855, 541, 461 cm⁻¹) due to one or both of these conformers. The dipole moment of these two conformers is 2.6-2.9D, as compared to 0.6D for the more stable form,² so the two G conformers are stabilized more in going from vapor to liquid than is the A conformer.

1,2-Dibromopropane-d₆

Infrared spectra were obtained for 1,2-dibromo-propane-d₆ liquid, unannealed solid, and annealed solid. Those spectra are not given here, but are available from the authors. The spectrum of the annealed solid shows the absence of several liquid-state bands, as expected, because the deuterated compound should behave like the protonated compound. However, most of the bands will be due to different mixtures of normal modes in the the two compounds because the C-D frequencies are lower than C-H.

The force constants that were obtained for CH₂BrCHBrCH₃ were used to calculate fundamental wave-numbers for CD₂BrCDBrCD₃. In the final computer run, the

TABLE 1
Observed and calculated wavenumbers and potential energy distribution
for 1,2-dibromopropane

Obs. ^a	P _X S _{HH} conformer			P _C S _{HH} conformer			P _B S _{HH} conformer		
	cm ⁻¹		P.E.D. (%) ^b	cm ⁻¹		P.E.D. (%) ^b	cm ⁻¹		P.E.D. (%) ^b
	calc.	P.E.D. (%) ^b	calc.	P.E.D. (%) ^b	calc.	P.E.D. (%) ^b	calc.	P.E.D. (%) ^b	
1453m	1453	3(92)		1453	3(93)		1452	3(93)	
1445s	1452	3(93)		1452	3(93)		1451	3(93)	
1430s	1432	5(74), 15(25)		1434	5(74), 15(25)		1431	5(75), 15(25)	
1378s	1380	4(89), 7(12)		1379	4(92), 6(10)		1378	4(97)	
1338m	1342	6(56), 4(16), 8(14), 2(10)		1336	6(63), 4(13), 7(10)				
1314s							1311	6(79)	
--				1271	8(53), 6(34)				
1243s							1236	8(85)	
1233s	1247	6(38), 7(34), 8(16), 2(11)					1214	7(56), 6(38)	
1227s									
1212s	1211	8(58), 6(29)					1204	6(44), 7(29), 2(24)	
--				1188	7(78), 6(12)				
--				1172	6(43), 8(37), 2(15)				
1156s	1162	7(59), 6(35)							
1120m	1113	2(69), 6(12), 10(11)		1107	2(55), 6(18), 10(14)		1111	2(61)	
1098w									
1056vw				1060	2(64), 10(11), 7(10)				
1038s	1049	2(43), 10(26), 9(12)					1023	2(35), 10(34)	
--									
1001s	987	10(73), 6(10)		1004	10(62), 9(11)				
984w							981	10(76)	
906w				914	10(50), 2(26)				
897s	897	10(45), 2(43)							
891w							898	2(48), 10(39)	

TABLE 1 (CONTINUED)

Obs. ^a	P _X S _{HF} conformer			P _C S _{HF} conformer			P _B S _{HF} conformer		
	cm ⁻¹	calc.	P.E.D. (%) ^b	calc.	P.E.D. (%) ^b	calc.	P.E.D. (%) ^b		
855m				853	9(65), 10(19)	846	9(71), 2(14)		
842m	839	9(64), 2(19)							
662w				664	1(46), 11(34)				
649s	652	1(50), 11(48), 2(11)							
564vs	565	1(96), 11(10)				583	1(64), 12(31), 11(29)		
541m				524	1(71), 12(27)				
526w						521	1(75), 11(35)		
461m						443	1(33), 12(27), 11(24)		
403m	407	12(57)							
359w				353	1(34), 11(25), 12(11), 2(10)				
338w				320	11(43), 12(42)	319	11(54), 1(22), 14(11)		
295m	282	11(65), 1(15), 12(10)				281	11(71), 12(11)		
270w				256	11(45), 13(23), 1(13)				
245vw	250	13(96)		251	13(72) 11(12)	248	13(97)		
187vw	179	11(38), 1(26)							
165vw	157	11(89), 12(15)		164	11(63) 14(40)				
-						140	11(42), 14(27), 12(15)		
115w	121	14(70), 9(13), 11(10)		74	11(75), 14(33)	77	14(43), 11(30), 12(11)		
85vw									

^aFrom Ref. 1.

^bContributions less than 10% are excluded. The coordinate numbers refer to the following definitions: 1 = C-Br stretch; 2 = C-C stretch; 3 = CH₃ antisym bend; 4 = CH₃ sym bend; 5 = CH₂ bend; 6 = C-H bend; 7 = CH₃ wag; 8 = CH₂ twist; 9 = CH₃ rock; 10 = CH₃ rock; 11 = CCB₂ bend; 12 = CCC bend; 13 = CH₃ torsion; 14 = CH₂Br torsion; 15 = CH₂ redundancy

TABLE 2
Observed and calculated wavenumbers and potential energy distribution
for 1,2-dibromopropane-d₆

Obs.	P _X S _{XX} conformer			P _C S _{HH} conformer			P _H S _{HH} conformer		
	cm ⁻¹	calc.	P.E.D. (%) ^a	cm ⁻¹	calc.	P.E.D. (%) ^a	cm ⁻¹	calc.	P.E.D. (%) ^a
1213s	1198	2(83)		1210	2(80), 6(23), 7(10)				
1183w ^b							1185	2(88), 6(21)	
1114ms	1111	2(54), 4(26), 7(12)		1116	2(54), 4(16), 11(14), 6(13)		1106	2(56), 4(25), 7(10)	
1049s	1046	3(94)		1052	3(55), 4(20), 7(12)		1047	3(95)	
	1046	3(96)		1046	3(93)		1046	3(94)	
--	1038	5(62), 16(18), 4(11)		1039	3(40), 4(36), 7(10)		1037	5(64), 16(21)	
--				1030	5(42), 16(16), 4(13), 6(11)				
1016m ^b							1020	4(64), 6(18)	
1002m	1017	4(60), 6(16)							
987w ^b							977	7(47), 6(40), 1(12)	
943w				940	7(50), 6(29)				
909sh	912	8(37), 7(14), 10(14), 12(10)		915	8(39), 10(16), 6(12), 12(10)		912	6(33), 10(15), 2(12)	
901s	901	6(50), 2(20)							
	896	7(49), 6(31), 10(13), 1(11)		890	6(30), 2(25), 7(10)				
845w	837	8(39), 6(18), 9(11)		834	8(50), 6(18), 10(13)		855	8(66)	
787mw				777	6(43), 10(27)		788	6(40), 7(25), 10(19)	
775m	769	10(41), 6(28), 8(10)					754	10(50), 6(24)	
744w ^b									

TABLE 2 (CONTINUED)

Obs.	P _X S _{HH} conformer			P _C S _{HH} conformer			P _H S _{HH} conformer		
	cm ⁻¹	calc.	P.E.D. (%) ^a	calc.	P.E.D. (%) ^a	calc.	P.E.D. (%) ^a		
731m	722	10(35), 2(26)		716	10(54), 7(16), 2(13)		726	10(41), 2(27)	
682w ^b							680	9(59), 10(15)	
664mw	659	9(54), 10(24)		657	9(52), 10(30)				
594s	576	1(39), 11(31), 10(24)				579	1(44), 11(24), 10(16)		
582mw									
528s	522	1(88)					517	1(53), 12(27), 11(26), 10(14)	
487m ^b							479	1(79), 11(16)	
-				471	1(71), 12(14), 9(12)				
420mw ^b							404	1(38), 11(20), 12(18)	
335mw	336	12(51), 11(25), 9(11), 10(10)		330	1(32), 11(28), 2(10)				
296w				290	12(50), 11(28), 1(12)				
261m	{ 254	11(64), 1(16)					270	11(62), 14(18), 1(16)	
no							252	11(76), 12(10)	
data	186	13(34), 11(26), 1(15)		176	13(96)		172	13(97)	
	173	13(40), 11(26), 1(22)							
	153	11(49), 13(23), 12(12)		146	11(62), 14(21)		140	11(31), 12(20), 14(16)	
	99	14(81), 11(52)		82	11(77), 14(15)		68	14(65), 11(50)	

^aSee footnote b, Table 1^bBands that are absent in the annealed solid. The solid-state spectrum was not obtained below 300 cm⁻¹.

same twenty force constants that were adjusted previously were adjusted to fit the fifty-eight assigned values for the three conformers of $\text{CH}_2\text{BrCHBrCH}_3$, and the forty-seven assigned values for the three conformers of $\text{CD}_2\text{BrCDBrCD}_3$. The average difference between observed and calculated wavenumbers for the 105 values was 6.6 cm^{-1} . The observed and calculated wavenumbers are given in Tables 1 and 2 for the two compounds, along with the approximate potential energy distributions, which are given in terms of ordinary symmetry coordinates. Symmetry coordinates were used as an aid in interpreting the spectra, even though the molecules have no symmetry.

Table 2 lists seven bands that were present in the spectrum of the liquid and unannealed solid, but were absent for the annealed solid of $\text{CD}_2\text{BrCDBrCD}_3$. It can be seen that all seven bands are assigned solely to the $\text{P}_\text{H}\text{S}_{\text{HH}}$ conformer (G. in TEKT notation). This conformer obviously disappears on annealing the solid. The spectrum of the annealed solid seems to indicate that the solid was amorphous rather than crystalline, and both the $\text{P}_\text{x}\text{S}_{\text{HH}}$ and $\text{P}_\text{C}\text{S}_{\text{HH}}$ conformers are present in the solid.

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