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Microwave and vibrational spectra, ab initio calculations, conformational stabilities and assignments of the fundamentals of the C_s conformer of *n*-butylsilane

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ABSTRACT

The vibrational spectrum of *n*-butylsilane is described. Complete assignments of fundamentals are made for the anti–anti (aa) conformer of C_s symmetry. The relative stabilities of the five different conformers are calculated, and the (aa) conformer emerges as the conformer of lowest relative energy, and thus the most abundant, entirely dominating the infrared and Raman spectra as confirmed by the spectra of the annealed crystal. The dipole moments of all the conformers are calculated to lie between 0.88 and 1 Debye, similar to the dipole moments of the conformers of *n*-butylgermane.

Microwave measurements of this molecule seeded in a molecular jet were made using Fourier-transform microwave spectroscopy and confirmed the presence of the aa conformer, in addition to the anti–gauche (ag) and gauche–anti (ag) conformers. Measurement of rotational spectra for all four ^{13}C-substituted isotopologues as well as the ^{29}Si and ^{30}Si species for the aa conformer allowed a heavy atom structure determination for this conformer.

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1. Introduction

As the vibrational spectrum of *n*-butylsilane should be analogous to that of *n*-butylgermane [1], a similar investigation of *n*-butylsilane was undertaken. This study should enable comparisons to be made between these two compounds, both in terms of conformational structure preferences as well as the torsional energetics required to convert one rotameric form to another. Furthermore, the results for both of these compounds can serve as a prelude to our current investigation into the conformational behavior of the analogous hydrocarbon, *n*-pentane. The vibrations of *n*-butylsilane were last studied by Murata et al. [2]. These authors presented very good spectroscopic results, but they had only the normal coordinate treatments of the era available to them to support their analyses. In our investigations, we use the Gaussian 03 suite of quantum chemical programs [3] to support our analyses, which provides a level of surety unavailable to the earlier workers. Additionally, the earlier workers confined their spectroscopic presentations to tabular form, and we present here complete infrared and Raman spectra of gas, liquid and solid, as well as tabulated frequencies and complete assignments for the C_s conformer. The relative energy between the C_s (aa) conformer and the C_1 (ag) conformer in the liquid is also reported, and is in good agreement with the relative energy determined from the ab initio calculations.

2. Experimental

The sample of *n*-butylsilane was purchased from Gelest [1] and used without further purification. The samples were distilled into sampling devices on an all glass vacuum line. The Raman spectrum of liquid *n*-butylsilane was obtained by sealing the distillate into a glass capillary chilled to liquid nitrogen temperatures and maintained under running vacuum. The same capillary was used to study the temperature dependence of the Raman spectrum of the liquid in a Harney–Miller cell cooled with liquid nitrogen boil off, and controlled by an Omega Engineering Inc. CNN 8202-T1-T2-C2 dual controller using type T thermocouple wire and operating a CSS-03130/120 30 watt cartridge heater immersed in the liquid nitrogen reservoir. With this controller, constant temperatures set down to −130 °C could be maintained for hours. The Raman spectrometer has been briefly described in an earlier publication

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Table 1
Observed infrared and Raman wavenumbers for *n*-butylsilane.

Infrared						Raman					Assignment
Gas	Rel. int.	Liquid	Rel. int.	Solid cryst.	Rel. int.	Liquid	Rel. int.	Solid cryst.	Rel. int.	ν_I	Conformer and S_i description
2978	m, sh										
2974.9 Q	s, sh	2974	s, sh*					2973	vw, sh		
2969.1 Q	vs										
2966.7	s, sh	2966	vvs*	2960	vs*	2965	sm	2964	vs	ν_1	aa A′ a CH_3 stretch
				2954	vs*			2954	m	ν_{27}	aa A″ a CH_3 stretch
		2945	vw*	2949	vs			2950	vvw		
2939	m, sh			2936	w, sh*	3938	vs	2938	m	ν_{28}	aa A″ a C(3)H_2 stretch
2935.0 Q	vs							2935	vw		
2927.8	vs sh	2928	vvs	2928	vs sh*			2928	ms		
				2925	vvs*			2927	m, sh	ν_{29}	aa A″ C(2)H_2 stretch
				2914	vvs*	2914	s	2918	m, sh	ν_2	aa A′ s CH_3 stretch
2905	vvw, sh	2905	vw*	2911	m, sh*			2911	ms	ν_{30}	aa A″ C(1)H_2 stretch
2891.3	m	2894	vw*	2895	vw, sh*	2894	vvs				
2886.4	w, sh			2887	s*			2889	vvs	ν_3	aa A′ s C(3)H_2 stretch
2880.9	ms			2882	s, sh*	2877	vs	2881	vw, sh		
2871	vw, sh	2874	vw*	2870	vs			2871	vs	ν_4	aa A′ s C(2)H_2 stretch
2867	vw, sh							2868	vvw, sh		
		2862	vs	2863	w, sh*	2861	s	2862	vvw, sh		
				2855	vs			2851	s	ν_5	aa A′ s C(1)H_2 stretch
2803	w, b, sh	2808	w, sh	2808	vw, sh	2805	wm, b				
				2800	wm	2798	wm, sh	2786	vw		
2166.6	vs	2167	s*	2167	vvs *						
2162.9 Q	vs	2163	w, sh*		*			2163	vvs	ν_6	aa A′ a SiH_3 stretch
2157.4 Q	vvs	2157	s*					2158	sm, sh		
2156	vvs, sh	2154	vvs	2154*	vvs*	2154	vvvs	2154	vvs	ν_7	aa A′ s SiH_3 stretch
					*			2150	m, sh		
				2143	vvs*			2147	vs	ν_{31}	aa A″ a SiH_3 stretch
1476 R	wm, sh										
1473.8 Q	wm			1473	vw, sh						
1472 P	w, sh										
1466.5 Q	mw, sh										
1463.7 Q	mw	1460	vs	1463	vvs			1462	vw, sh	ν_8	aa A′ C(1)H_2 deformation
1457 P	w, sh			1455.2	vvs			1456.7	vs	ν_9	aa A′ a CH_3 deformation
1451	w, sh	1448	w, sh	1452	vvw, sh	1451	ms	1451.7	m, sh		
				1439	vvw			1441	mw	ν_{32}	aa A″ a CH_3 deformation
				1434	ms			1432.3	m	ν_{10}	aa A′ C(2)H_2 deformation
1419	vw, sh					1419	mw, sh				
1413	vw, sh	1416	sm	1415	vs	1413	vw, sh	1414.8	wm	ν_{11}	aa A′ C(3)H_2 deformation
1390.5 R	w			1396.4	vs			1397	w	ν_{12}	aa A′ s CH_3 deformation
1384.3 Q	wm	1384	vs	1385	w			1387	vvw		
1381 P	w, sh	1380	vs	1373.7	s	1375	vw	1375	vvw	ν_{13}	aa A′ C(2)H_2 wag
1365.6 Q	vw			1365	wm			1365	vvw		
1361	vw, sh	1361	m	1356	w	1361	w, sh	1357	w		
1352.1 R	w										
1345.7 Q	w			1349	vvw						
1341 P	vw, sh	1343	s	1339	vw	1342	w				
				1334.6	vw						
1305.3 R	w			1305.3	w	1306	mw	1305.3	sm	ν_{14}	aa A′ C(1)H_2 wag
1302.3 Q	w										
1297.4 P	w	1296.5	s	1294.7	sm	1292	mw, sh	1296	w		
1279	vw, sh			1274.8	m			1277	vvw	ν_{33}	aa A″ C(1)H_2 twist
1198.7	w			1198.1	sm			1199.6	w, sh	ν_{35}	aa A″ op CH_3 rock
1189.4	wm	1188.1	s	1186.7	s	1190	sm	1187.8	s	ν_{15}	aa A′ C(3)H_2 wag
1175	vw, sh	1178.3	s	1180	vvw, sh	1174	vw, sh				
1121	vvw, sh			1116	w	1123	w				
1091.8	wm										
1087.8	wm	1086	vs	1086.6	vs	1085	mw	1086.3	wm	ν_{16}	aa A′ ip CH_3 rock
1083.4	mw			1084.2	vs						
1082.6	mw	1079	w, sh	1079	mw						
				1052.9	m	1052	m	1053.8	ms	ν_{17}	aa A′ a CCC stretch
1041	w, sh			1041.5	ms			1045	w, sh		
1036	wm					1035	mw, sh				ag a CCC stretch
1030.7 Q	mw	1028	s	1026.8	vs			1025	w	ν_{36}	aa A″ C(3)H_2 twist
1002	vvw	1002.5	w	1003.2	sm	1003	w, sh	1004.5	wm	ν_{18}	aa A′ a CCC stretch
				994	vw, sh						ag s CCC stretch
		970.6	s			964	vvw, sh				
948	vvw			943	vvs*	945	s	941.4	vs sh	ν_{19}	aa A′ a SiH_3 deformation
938.3	vvs	938.3	vvs					938.4	vvs, sh	ν_{37}	aa A″ a SiH_3 deformation
932.3	vs	930	vvs					931.8	m	ν_{20}	aa A′ s SiH_3 deformation
				926	vvs**	926	vvw, sh				ag a SiH_3 deformation
		902	vs	909	vvs*			913	w	ν_{38}	aa A″ C(3)H_2 rock
892.3	mw							892	vvw, sh		

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