Journal of Molecular Structure 934 (2009) 66–78

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

The r_0 structural parameters, conformational stability, and vibrational assignment of equatorial and axial bromocyclobutane

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ARTICLE INFO

Article history:
Received 23 May 2009
Accepted 17 June 2009
Available online 21 June 2009

Keywords:
Conformational stability
r_0 Parameters
Infrared spectrum
Xenon solutions
Bromocyclobutane

ABSTRACT

Variable temperature (−55 to −100 °C) studies of the infrared spectra (3500–400 cm^{-1}) of bromocyclobutane, c-C_4H_7Br, dissolved in liquid xenon have been carried out as well as the infrared spectra of the gas and solid and Raman spectrum of the liquid. By utilizing eight pairs of conformers at ten different temperatures, the enthalpy difference between the more stable equatorial conformer and the axial form has been determined to be 291 ± 22 cm^{-1} (3.48 ± 0.26 kJ/mol). The percentage of the axial conformer present at ambient temperature is estimated to be 20 ± 1%. The *ab initio* MP2(full) average predicted energy difference from a variety of basis sets is 560 ± 46 cm^{-1} (6.70 ± 0.55 kJ/mol) and the average value of 569 ± 47 cm^{-1} from density functional theory predictions by the B3LYP method are significantly larger than the experimentally determined enthalpy differences. By utilizing previously reported microwave rotational constants for the equatorial conformer combined with *ab initio* MP2(full)/6-311+G(d,p) predicted structural values, adjusted r_0 parameters have been obtained. The determined heavy atom structural parameters for the equatorial conformer are: distances (Å) C–Br = 1.942(3), C_α–C_β = 1.541(3), C_β–C_γ = 1.552(3) and angles (°) $\angle C_\alpha C_\beta C_\gamma$ = 86.8(5), $\angle C_\beta C_\alpha C_\beta$ = 89.7(5), $\angle$Br–($C_\beta C_\alpha C_\beta$) = 132.1(5) and a puckering angle of 29.8(5). The conformational stabilities, harmonic force fields, infrared intensities, Raman activities, depolarization ratios and vibrational frequencies have been obtained for both conformers from MP2(full)/6-31G(d) *ab initio* calculations and compared to experimental values where available. The results are discussed and compared to the corresponding properties of some similar molecules.

1. Introduction

Very limited structural data have been obtained for monosubstituted cyclobutane and the first study using microwave spectra was for bromocyclobutane [1] with a more extensive one for chlorocyclobutane [2]. In this later investigation [2], only the equatorial conformer was assigned for the normal species and eight of its isotopomers. The isotopomers were β-^{13}C and three isotopomers with deuterium substitutions (d_1, d_2 and d_5) which were α-d and β-d_2, as well as α-d, β-d_2 and β′-d_2 for the ^{35}Cl isotope and only the three deuterium isotopomers for ^{37}Cl. In this study all fourteen structural parameters were determined assuming the equatorial and axial CH distances on the same carbon had the same values. However, the determined values for the CH distances ranged from 1.090 to 1.110 Å which is a very large difference. A later effort [3] was made utilizing *ab initio* calculations and the experimentally determined rotational constants to determine the r_0 structural parameters more accurately by utilization of the diagnostic least squares method [4]. However a satisfactory fit of the A rotational constants for several of the isotopomers could not be achieved. In the same study [3], *ab initio* calculations were utilized to predict the structural parameters of the higher energy axial conformer which subsequently Caminati et al. [5] used to identify and assign the spectrum of the axial conformer. In this new investigation, values of the A rotational constants for both the ^{35}Cl and ^{37}Cl isotopomers of the equatorial conformer were reported which were significantly different from those initially reported [2]. Therefore, we recently used these new values to obtain [6] r_0 structural parameters for the equatorial and axial conformers by combining the rotational constants obtained from these experimental studies [5] coupled with the MP2(full)/6-311+G(d,p) *ab initio* calculations.

As a continuation of our conformational and structural determination of monosubstituted cyclobutanes [6–9] we have investigated the infrared and Raman spectra of bromocyclobutane. The microwave spectrum was recorded by Rothschild and Dailey [1] but only the spectrum of equatorial conformer was identified and assigned. However, Rothschild [10] later reported vibrational evidence for the axial conformer from temperature studies of the infrared spectrum from which a potential for the ring puckering

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[1] Taken in part from the thesis of Joshua J. Klaassen, which will be submitted in partial fulfillment of the Ph.D. degree.

[2] Taken in part from the thesis of Arindam Ganguly, which will be submitted in partial fulfillment of the Ph.D. degree.

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doi:10.1016/j.molstruc.2009.06.017

Table 1
Observed[a] and calculated[b] frequencies for the *equatorial* conformer of bromocyclobutane.

		Fundamental	*Ab initio*	Fixed scaled[c]	IR int.	Raman act.	dp ratio	IR gas	Raman gas[d]	IR Xe Soln.	Raman liquid[e]	IR solid	Raman solid[d]	P.E.D.[f]	Band contour		
															A	B	C
A′	ν_1	β-CH_2 antisymmetric stretch	3215	3016	28.5	43.4	0.61	3005	–	2996	–	3003/2993	–	$66S_1,28S_2$	59	–	41
	ν_2	γ-CH_2 antisymmetric stretch	3196	2998	5.0	82.0	0.43	2996	–	–	–	–	2994	$70S_2,22S_1$	3	–	97
	ν_3	CH stretch	3177	2980	1.6	71.6	0.49	2988	–	–	–	–	2980	$87S_3,12S_1$	74	–	26
	ν_4	β-CH_2 symmetric stretch	3140	2946	4.7	199.0	0.05	2962	–	2950	2945	2950/2946	2945	$86S_4,12S_5$	–	–	100
	ν_5	γ-CH_2 symmetric stretch	3136	2942	22.9	67.7	0.44	2931	–	2918	2912	2916/2906	2906	$87S_5,13S_4$	96	–	4
	ν_6	β-CH_2 scissors	1574	1477	1.8	6.7	0.64	1476	~1470	1464	1460	1461/1459	1458	$64S_6,34S_7$	99	–	1
	ν_7	γ-CH_2 scissors	1549	1453	5.4	18.1	0.74	1452	1449	1445	1438	1441/1434	1443	$65S_7,34S_6$	16	–	84
	ν_8	β-CH_2 wag	1339	1270	50.0	7.4	0.62	1263	1262	1257	1252	1264/1254	1255	$50S_8,28S_9$	15	–	85
	ν_9	CH in-plane bend	1299	1232	5.9	5.8	0.74	1235	1234	1232	1227	1236/1232	1233	$22S_9,29S_8,28S_{10},10S_{13}$	100	–	–
	ν_{10}	β-CH_2 twist	1262	1197	10.3	6.6	0.75	1199	1204	1195	1190	1204/1194	1195	$46S_{10},18S_{15},11S_9$	59	–	41
	ν_{11}	β-CH_2 rock	1156	1097	2.5	3.7	0.21	1093	1091	1088	1084	1090/1085	1090	$33S_{11},25S_{12},13S_{17}$	73	–	27
	ν_{12}	Ring breathing	1070	1015	6.6	10.7	0.20	1017	1016	1014	1012	1016/1014	1016	$67S_{12},14S_{11}$	57	–	43
	ν_{13}	Ring deformation 1	955	906	0.5	2.0	0.42	900	–	900	–	906/902	905	$55S_{13},15S_{15},13S_8$	96	–	4
	ν_{14}	Ring deformation 2	864	820	39.4	8.9	0.17	827	824	818	808	811/802	803	$34S_{14},20S_{15},16S_{13},11S_{16}$	26	–	74
	ν_{15}	γ-CH_2 rock	729	692	12.2	6.1	0.24	701	701	700	698	702/699	701	$32S_{15},29S_{14},13S_{16}$	100	–	–
	ν_{16}	C–Br stretch	508	482	1.8	5.5	0.33	487	486	487	481	485/476	484	$26S_{16},22S_{14},17S_{11},12S_9,11S_{17}$	84	–	16
	ν_{17}	C–Br in-plane bend	318	302	3.9	5.4	0.29	302	301		298	299	303	$21S_{17},17S_{18},46S_{16}$	97	–	3
	ν_{18}	Ring puckering	170	161	0.6	1.1	0.28	–	150		150	–	175	$60S_{18},21S_{16},16S_9$	100	–	–
A″	ν_{19}	β-CH_2 antisymmetric stretch	3206	3007	15.1	62.5	0.75	2993		2986	2977	2983/2980	2971	$100S_{19}$	–	100	–
	ν_{20}	β-CH_2 symmetric stretch	3138	2944	28.2	2.2	0.75	2975		2963	–	2971/2969	2960	$100S_{20}$	–	100	–
	ν_{21}	β-CH_2 scissors	1540	1445	2.6	5.9	0.75	1442		1437	1438	1438/1425	1434	$99S_{21}$	–	100	–
	ν_{22}	CH out-of-plane bend	1334	1266	1.7	5.6	0.75	1280		1277	–	1271/1259	1270	$47S_{22},29S_{23},10S_{29}$	–	100	–
	ν_{23}	γ-CH_2 wag	1293	1227	0.8	0.3	0.75	1228		1228	1227	1227/1221	1226	$29S_{23},24S_{27},18S_{25},17S_{22},11S_{24}$	–	100	–
	ν_{24}	β-CH_2 wag	1282	1216	0.01	2.7	0.75	–		1218	–	–	1220	$43S_{24},20S_{23},19S_{25},12S_{22}$	–	100	–
	ν_{25}	γ-CH_2 twist	1224	1161	2.1	10.0	0.75	1161		1161	1160	1166/1160	1166	$29S_{25},39S_{24},11S_{26}$	–	100	–
	ν_{26}	Ring deformation 1	1087	1031	0.1	1.2	0.75	–		1030	1025	1031/1020	1034	$27S_{26},34S_{28},28S_{27}$	–	100	–
	ν_{27}	β-CH_2 twist	982	932	2.1	0.3	0.75	938		937	933	942/938	940	$34S_{27},21S_{22},20S_{26},16S_{25}$	–	100	–
	ν_{28}	Ring deformation 2	958	909	0.6	10.2	0.75	907		891	896	896/892	896	$58S_{28},24S_{26}$	–	100	–
	ν_{29}	β-CH_2 rock	818	776	1.3	0.8	0.75	786		778	785	785/778	779	$78S_{29},13S_{25}$	–	100	–
	ν_{30}	C–Br out-of-plane bend	259	246	0.2	1.6	0.75	245			249	249	255	$91S_{30}$	–	100	–

[a] Observed spectra: gas, Xe, and solid are IR while liquid is Raman.

[b] MP2(full)/6-31G(d) *ab initio* calculations, scaled frequencies, infrared intensities (km/mol), Raman activities (Å^4/u), depolarization ratios (dp) and potential energy distributions (P.E.D.s).

[c] Scaled frequencies with scaling factors of 0.88 for the CH stretches, β-CH_2 and γ-CH_2 scissors and 0.90 for all other modes.

[d] Frequencies listed are taken from reference [12].

[e] Frequencies listed are taken from reference [11].

[f] Symmetry coordinates with P.E.D. contribution less than 10% are omitted.

mode was proposed. Since that time there have been extensive vibrational studies of bromocyclobutane with two of the investigations [11,12] emphasizing the vibrational assignment. In the first study [11], three different deuterated isotopes were utilized to dis-