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An DFT studies of conformational stability, vibrational frequencies and normal mode analysis of 3-bromo-1-butene

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Abstract

The conformational stability, vibrational frequencies and corresponding normal mode analysis for all three conformers of 3-bromo-1-butene, $\text{H}_2\text{C}=\text{CHCH}(\text{CH}_3)\text{Br}$, were investigated using the 6-311++G(d,p) basis set by the BLYP and B3LYP methods. From the calculations, the enthalpy differences (ΔH) between the most stable HE (hydrogen atom eclipses the double bond) and the higher energy ME (methyl group eclipses the double bond) conformations have been obtained to be 4.20 (BLYP) and 3.74 kJ mol^{-1} (B3LYP). The same calculation yields a ΔH of 11.25 (BLYP) and 9.64 kJ mol^{-1} (B3LYP) between the HE and the least stable BrE (bromine atom eclipses the double bond) form. The normal mode analysis for vibrational frequencies is proposed for all three conformers using the force constants from BLYP/6-311++G(d,p) calculations. Additionally, the complete equilibrium geometries, the infrared intensities and the Raman activities were also obtained from the calculations.

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Keywords: 3-Bromo-1-butene; Conformational stability; Enthalpy difference; Normal mode analysis

1. Introduction

The conformational stabilities of 3-halo-1-butenes, $\text{CH}_2=\text{CHCH}(\text{CH}_3)\text{X}$ ($\text{X}=\text{F}$, Cl), have been interested to chemists because three possible conformers coexist in the fluid phases at ambient temperature [1,2]. The conformational stability among conformers of 3-fluoro-1-butene, $\text{CH}_2=\text{CHCH}(\text{CH}_3)\text{F}$, has been determined the conformer HE (hydrogen atom eclipses the double bond) for the most stable one, the conformer XE (halogen atom eclipses the double bond) for the second most one and the conformer ME (methyl group eclipses the double bond) for the least stable one [1]. However, the stability of 3-chloro-1-butene, $\text{CH}_2=\text{CHCH}(\text{CH}_3)\text{Cl}$, has been determined the HE for the most stable conformer, the ME for the second one and the XE for the least one [2].

Therefore, we were interested in investigating the conformational stability of 3-bromo-1-butene, $\text{CH}_2=\text{CHCH}(\text{CH}_3)\text{Br}$, where the bromine atom provides

larger steric hindrance and weaker electronegativity than the fluorine and the chlorine atom does. To determine the conformational stability of 3-bromo-1-butene we have carried out molecular geometry optimization calculations for all the three conformations using the 6-311++G(d,p) basis set with the BLYP and B3LYP methods. In order to provide a complete description of the molecular motions involved in the normal modes of these conformers we have also carried out the frequency calculations using the 6-311++G(d,p) basis set with the BLYP and B3LYP methods. The results of this study are reported herein.

2. Calculations

In this study the density functional theory with the Becke's exchange functional (BLYP) [3] and the Becke's three parameter exchange functional [4] and correlation functional by Lee et al. [5] (B3LYP) calculations were carried out with the GAUSSIAN-98 program [6] using Gaussian-type functions. The energy minima with respect to the nuclear coordinates were obtained by the simultaneous relaxation of all the geometrical parameters of the molecule using the gradient method of Pulay [7].

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Table 1

Structural parameters, rotational constants, dipole moments and total energies for the conformer with the H₆ hydrogen atom eclipsing the double bond (HE) of 3-bromo-1-butene

Parameter ^a	BLYP/6-311 + +G(d,p)			B3LYP/6-311 + +G(d,p)		
	HE	ME	BrE	HE	ME	BrE
$r(\text{C}_2=\text{C}_1)$	1.343	1.343	1.338	1.332	1.332	1.328
$r(\text{C}_3-\text{C}_2)$	1.494	1.498	1.509	1.489	1.494	1.501
$r(\text{Br}-\text{C}_3)$	2.070	2.076	2.034	2.028	2.031	2.000
$r(\text{C}_5-\text{C}_3)$	1.530	1.526	1.537	1.521	1.517	1.527
$r(\text{H}_6-\text{C}_3)$	1.095	1.096	1.098	1.089	1.090	1.092
$r(\text{H}_7-\text{C}_1)$	1.092	1.090	1.089	1.086	1.084	1.083
$r(\text{H}_8-\text{C}_1)$	1.090	1.090	1.090	1.084	1.084	1.084
$r(\text{H}_9-\text{C}_2)$	1.094	1.093	1.098	1.087	1.086	1.091
$r(\text{H}_{10}-\text{C}_5)$	1.098	1.098	1.098	1.092	1.091	1.091
$r(\text{H}_{11}-\text{C}_5)$	1.102	1.102	1.103	1.095	1.095	1.096
$r(\text{H}_{12}-\text{C}_5)$	1.097	1.096	1.097	1.091	1.090	1.091
$\angle(\text{C}_3-\text{C}_2=\text{C}_1)$	124.0	125.8	129.5	123.9	125.6	129.3
$\angle(\text{Br}-\text{C}_3-\text{C}_2)$	107.9	107.2	113.1	108.2	107.5	113.1
$\angle(\text{C}_5-\text{C}_3-\text{C}_2)$	114.7	118.0	113.0	114.2	117.4	112.6
$\angle(\text{H}_6-\text{C}_3-\text{C}_2)$	111.5	110.3	109.7	111.0	109.9	109.3
$\angle(\text{H}_7-\text{C}_1=\text{C}_2)$	121.7	122.7	121.9	121.8	122.7	122.0
$\angle(\text{H}_8-\text{C}_1=\text{C}_2)$	121.4	120.8	120.6	121.4	120.7	120.5
$\angle(\text{H}_9-\text{C}_2=\text{C}_1)$	120.1	119.4	118.9	120.2	119.5	118.9
$\angle(\text{H}_{10}-\text{C}_5-\text{C}_3)$	111.3	111.8	111.0	111.2	111.6	110.9
$\angle(\text{H}_{11}-\text{C}_5-\text{C}_3)$	108.8	109.3	109.1	108.9	109.4	109.2
$\angle(\text{H}_{12}-\text{C}_5-\text{C}_3)$	111.3	110.7	111.2	111.3	110.6	111.2
$\tau(\text{Br}-\text{C}_3-\text{C}_2=\text{C}_1)$	112.7	−119.2	−1.9	114.1	−121.0	−1.8
$\tau(\text{C}_5-\text{C}_3-\text{C}_2=\text{C}_1)$	−126.8	3.8	122.3	−125.0	2.3	122.4
$\tau(\text{H}_6-\text{C}_3-\text{C}_2=\text{C}_1)$	1.5	133.2	−114.5	2.1	130.2	−1145.0
$\tau(\text{H}_7-\text{C}_1=\text{C}_2-\text{C}_3)$	−2.5	1.2	0.3	−2.3	1.2	0.3
$\tau(\text{H}_8-\text{C}_1=\text{C}_2-\text{C}_3)$	177.8	−178.5	−179.7	178.0	−178.6	−179.7
$\tau(\text{H}_9-\text{C}_2=\text{C}_1-\text{C}_3)$	−178.1	179.0	179.7	−178.3	179.0	179.7
$\tau(\text{H}_{10}-\text{C}_5-\text{C}_3-\text{Br})$	64.4	68.7	64.4	64.0	63.4	64.1
$\tau(\text{H}_{11}-\text{C}_5-\text{C}_3-\text{H}_{10})$	119.2	120.2	119.2	119.2	120.2	119.2
$\tau(\text{H}_{12}-\text{C}_5-\text{C}_3-\text{H}_{10})$	−121.3	−120.8	−121.5	−121.1	−120.7	−121.3
<i>A</i>	4806.2	5741.0	4217.3	4933.1	5905.2	4288.3
<i>B</i>	1853.5	1733.8	2271.7	1889.4	1771.2	2328.6
<i>C</i>	1424.0	1442.2	1568.0	1455.4	1472.6	1603.5
μ	2.449	2.427	2.227	2.385	2.355	2.207
$-(E+2728)$	2.725409	2.723810	2.721124	2.817307	2.815883	2.813636
ΔE (kJ mol ^{−1})	0	4.20	11.25	0	3.74	9.64

Bond length in Å, bond angle in degrees, rotational constant (*A*, *B*, *C*) in MHz, dipole moment (μ) in debye and energy (*E*) in hartree.

^a For the definition of atom numbers, see Fig. 1.

The calculated structural parameters, rotational constants, dipole moments and total energies as determined with the 6-311 + +G(d,p) basis set are listed in Table 1 for all three conformers.

To obtain a complete description of the molecular motions involved in the normal modes of 3-bromo-1-butene we have carried out a normal mode analysis. This analysis was performed utilizing ab initio calculations and the Wilson matrix method [8]. The force field in Cartesian coordinates was calculated by the GAUSSIAN-98 program [6] using the 6-311 + +G(d,p) basis set by the BLYP and B3LYP methods, which gives more accurate spectroscopic properties [9–12] of organic compounds. Internal coordinates (Table 2 and Fig. 1) were used to calculate the *G* and *B* matrixes using the structural parameters given in Table 1. Using the *B* matrix [8] the force field in Cartesian coordinates was converted to a force field in the desired

internal coordinates [13] and the pure ab initio vibrational frequencies were reproduced. The force constants for all the three conformers of this molecule can be obtained from the author. A set of local symmetry coordinates for various subgroups (Table 3) was used to determine the corresponding potential energy distribution (PED). The calculated frequencies of the three conformers of 3-bromo-1-butene along with the calculated infrared intensities, Raman activities, and PED are given in Tables 4–6.

3. Results and discussion

3.1. Conformational stability and structural differences

From the total energies obtained by BLYP/6-311 + +G(d,p) and B3LYP/6-311 + +G(d,p) the conformational

Table 2
Internal coordinate definitions for 3-bromo-1-butene

Definition	Coordinate involved	Definition	Coordinate involved
R_1	C=C stretch	α_7	C ₂ C ₃ Br bend
R_2	C ₂ C ₃ stretch	α_8	C ₂ C ₃ C ₅ bend
R_3	C ₂ Br stretch	α_9	C ₂ C ₃ H ₆ bend
R_4	C ₃ C ₅ stretch	α_{10}	BrC ₃ C ₅ bend
R_5	C ₃ H ₆ stretch	α_{11}	BrC ₃ H ₆ bend
R_6	C ₁ H ₇ stretch	α_{12}	C ₅ C ₃ H ₆ bend
R_7	C ₁ H ₈ stretch	α_{13}	C ₃ C ₅ H ₁₀ bend
R_8	C ₂ H ₉ stretch	α_{14}	C ₃ C ₅ H ₁₁ bend
R_9	C ₅ H ₁₀ stretch	α_{15}	C ₃ C ₅ H ₁₂ bend
R_{10}	C ₅ H ₁₁ stretch	α_{16}	H ₁₀ C ₅ H ₁₁ bend
R_{11}	C ₅ H ₁₂ stretch	α_{17}	H ₁₀ C ₅ H ₁₂ bend
α_1	C=CH ₇ bend	α_{18}	H ₁₁ C ₅ H ₁₂ bend
α_2	C=CH ₈ bend	β_1	H ₇ C ₁ C ₂ H ₃ out-of-plane bend
α_3	H ₇ C ₁ H ₈ bend	β_2	H ₈ C ₁ C ₂ H ₃ out-of-plane bend
α_4	C=CC ₃ bend	β_3	H ₉ C ₂ C ₁ H ₃ out-of-plane bend
α_5	C=CH ₉ bend	τ_1	CH ₃ torsion
α_6	C ₃ C ₂ H ₉ bend	τ_2	Asymmetric torsion

For atom denotation, see Fig. 1.

stability among the conformers of 3-bromo-1-butene were determined as the HE form for the most stable, the ME the second and the BrE the third. The value of the ΔH between the HE and ME is about 4.20 and 3.74 kJ mol⁻¹ and those between the HE and BrE from 11.25 to 9.64 kJ mol⁻¹ at the BLYP/6-311 + + G(d,p) and B3LYP/6-311 + + G(d,p), respectively. The ΔH value between the HE and XE of 3-bromo-1-butene is significantly larger than those of 3-fluoro-1-butene [1] and 3-chloro-1-butene [2].

The most significant structural differences among the three conformers of 3-bromo-1-butene appeared on the parameters closest to the axis of internal rotation (Table 1). The bond lengths of the C–Br, C₃–C₅, C–H₆ bonds of the molecule are the shortest for the conformations in which these bonds eclipse the double bond same as those of 3-fluoro-1-butene [1] and 3-chloro-1-butene [2]. The C₂–C₃ bond, which is the axis bond of internal rotation, becomes longer in the order of size eclipsing atom/group. The C₂–C₃–Br bond angle of the BrE (bromine atom eclipses the double bond) form and the C₂–C₃–C₅ angle of the ME form

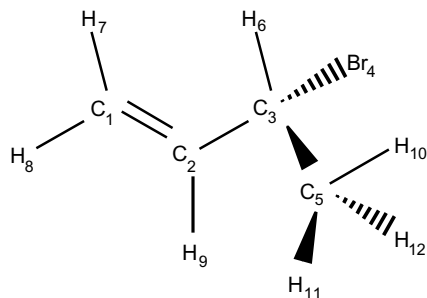


Fig. 1. Structural model and atom numbering of 3-bromo-1-butene.

Table 3
Symmetry coordinates for 3-bromo-1-butene

Description	Symmetry coordinate ^a
=CH ₂ antisymmetric stretch	$S_1 = R_6 - R_7$
=CH stretch	$S_2 = R_8$
=CH ₂ symmetric stretch	$S_3 = R_6 + R_7$
CH ₃ antisymmetric stretch	$S_4 = 2R_9 - R_{10} - R_{11}$
CH stretch	$S_5 = R_5$
CH ₃ antisymmetric stretch	$S_6 = R_{10} - R_{11}$
CH ₃ symmetric stretch	$S_7 = R_9 + R_{10} + R_{11}$
C=C stretch	$S_8 = R_1$
CH ₃ antisymmetric deformation	$S_9 = \alpha_{16} - \alpha_{17}$
CH ₃ antisymmetric deformation	$S_{10} = 2\alpha_{18} - \alpha_{16} - \alpha_{17}$
=CH ₂ deformation	$S_{11} = 2\alpha_3 - \alpha_1 - \alpha_2$
CH ₃ symmetric deformation	$S_{12} = \alpha_{13} + \alpha_{14} + \alpha_{15} - \alpha_{16} - \alpha_{17} - \alpha_{18}$
CH bend	$S_{13} = \alpha_9 - \alpha_{12}$
=CH bend, in-plane	$S_{14} = \alpha_5 - \alpha_6$
CH bend	$S_{15} = 2\alpha_{11} - \alpha_9 - \alpha_{12}$
CCC antisymmetric stretch	$S_{16} = R_2 - R_4$
CH ₃ rock	$S_{17} = 2\alpha_{13} - \alpha_{14} - \alpha_{15}$
CH ₃ rock	$S_{18} = \alpha_{14} - \alpha_{15}$
=CH bend, out-of-plane	$S_{19} = \beta_3$
=CH ₂ rock	$S_{20} = \alpha_1 - \alpha_2$
=CH ₂ twist	$S_{21} = \beta_1 + \beta_2$
CCC symmetric stretch	$S_{22} = R_2 + R_4$
=CH ₂ wag	$S_{23} = \beta_1 - \beta_2$
C=CC bend	$S_{24} = 2\alpha_4 - \alpha_5 - \alpha_6$
CBr stretch	$S_{25} = R_3$
CCC bend	$S_{26} = \alpha_8$
CBr bend	$S_{27} = \alpha_7 + \alpha_{10}$
CH ₃ torsion	$S_{28} = \gamma_1$
CBr bend	$S_{29} = \alpha_7 + \alpha_{10}$
Asymmetric torsion	$S_{28} = \gamma_2$

^a Not normalized.

are 3 and 6° larger than the C₂–C₃–H₆ angle of the HE form, respectively. The C₁=C₂–C₃ angle opens by 2 and 5° on conversion from the HE to the ME and to the BrE, respectively. When we compared the structural parameters with those of 3-fluoro-1-butene [1] and 3-chloro-1-butene [2], we could find that the angle opening of the C₁=C₂–C₃ became larger in the order of 3-fluoro-1-butene, 3-chloro-1-butene and 3-bromo-1-butene and the C₃–C₅ length of the bromine compound is about 0.003 and 0.008 Å longer than that of the chlorine and the fluorine ones, respectively.

3.2. Normal mode analysis

On the basis of our normal coordinate calculations, we suggested the vibrational modes of the fundamental harmonic frequencies (Tables 4–6). We shall discuss here only the modes that are at variance with a series of molecules of 3-fluoro-1-butene [1] and 3-chloro-1-butene [2]. The frequency region and order of the CH stretches and deformations are essentially the same as the modes for the equivalent molecules of 3-fluoro-1-butene [1] and 3-chloro-1-butene [2]. As an exception the order of vibrational frequency of CH stretching mode for the HE and ME conformers of bromine molecule was predicted to be located at the higher vibrational number of five than the order of

Table 4
Calculated wavenumbers (cm^{-1}) and potential energy distributions (PED) for the conformer with the H_6 hydrogen atom eclipsing the double bond (HE) of 3-bromo-1-butene

Vib. no.	Description	BLYP/6-311 + +G(d,p)					B3LYP/6-311 + +G(d,p)				
		cm^{-1}	IR int ^a	Raman act. ^b	dp ratio	PED	cm^{-1}	IR int ^a	Raman act. ^b	dp ratio	PED
1	=CH ₂ antisymmetric stretch	3140	11.8	96.2	0.60	96S ₁	3219	9.9	86.8	0.60	96S ₁
2	=CH stretch	3065	7.4	77.0	0.32	85S ₂	3145	5.4	74.6	0.30	87S ₂
3	=CH ₂ symmetric stretch	3056	11.3	116.1	0.12	90S ₃	3132	9.6	110.7	0.12	89S ₃
4	CH ₃ antisymmetric stretch	3047	10.4	42.7	0.30	50S ₄ , 23S ₆ , 19S ₅	3123	9.6	34.4	0.31	46S ₄ , 23S ₅ , 21S ₆
5	CH stretch	3031	4.5	81.8	0.49	64S ₅ , 26S ₆	3109	5.7	77.1	0.51	60S ₅ , 31S ₆
6	CH ₃ antisymmetric stretch	3013	9.0	101.1	0.54	40S ₆ , 42S ₄ , 11S ₇	3091	7.8	92.5	0.60	40S ₆ , 45S ₄
7	CH ₃ symmetric stretch	2950	18.5	216.1	0.08	87S ₇ , 11S ₆	3027	16.7	187.9	0.05	92S ₇
8	C=C stretch	1626	2.0	126.8	0.18	68S ₈ , 16S ₁₁	1692	2.5	114.5	0.16	69S ₈ , 14S ₁₁
9	CH ₃ antisymmetric deformation	1457	2.5	9.7	0.72	67S ₉ , 23S ₁₀	1493	2.4	9.1	0.71	69S ₉ , 22S ₁₀
10	CH ₃ antisymmetric deformation	1449	9.5	9.5	0.61	65S ₁₀ , 21S ₉	1486	10.3	8.8	0.63	67S ₁₀ , 19S ₉
11	=CH ₂ deformation	1419	8.5	32.4	0.29	70S ₁₁ , 12S ₁₄	1456	9.6	25.1	0.29	71S ₁₁ , 11S ₁₄
12	CH ₃ symmetric deformation	1374	6.7	2.4	0.69	98S ₁₂	1413	7.3	1.4	0.68	97S ₁₂
13	CH bend	1299	2.2	23.8	0.34	53S ₁₃ , 15S ₈ , 10S ₁₁ , 10S ₄	1335	1.6	20.9	0.36	54S ₁₃ , 14S ₈ , 11S ₁₁
14	=CH bend, in-plane	1284	2.0	7.6	0.25	54S ₁₄ , 18S ₁₃ , 11S ₂₀	1317	1.6	7.7	0.27	55S ₁₄ , 16S ₁₃ , 12S ₂₀
15	CH bend	1188	14.3	6.1	0.75	41S ₁₅ , 14S ₂₀ , 12S ₁₇	1228	22.6	5.8	0.68	53S ₁₅ , 11S ₂₀ , 10S ₁₇
16	CCC antisymmetric stretch	1140	37.7	26.1	0.34	18S ₁₆ , 32S ₁₅ , 21S ₁₈	1182	32.1	22.4	0.37	19S ₁₆ , 24S ₁₅ , 20S ₁₈
17	CH ₃ rock	1057	3.3	3.8	0.50	19S ₁₇ , 39S ₁₆ , 13S ₁₅ , 10S ₂₂	1097	2.9	3.9	0.47	20S ₁₇ , 40S ₁₆ , 11S ₂₂ , 10S ₁₅
18	CH ₃ rock	1004	31.6	4.6	0.32	45S ₁₈ , 13S ₁₉ , 13S ₂₀	1038	36.9	6.0	0.36	42S ₁₈ , 24S ₁₉
19	=CH bend, out-of-plane	988	12.4	1.5	0.68	68S ₁₉ , 16S ₂₃	1021	7.0	1.1	0.75	59S ₁₉ , 17S ₂₃
20	=CH ₂ rock	952	7.7	2.2	0.23	21S ₂₀ , 28S ₁₇ , 15S ₁₆	980	9.6	1.7	0.22	24S ₂₀ , 30S ₁₇ , 12S ₁₆ , 10S ₁₆
21	=CH ₂ twist	917	39.4	2.5	0.64	98S ₂₁	957	42.6	2.7	0.66	96S ₂₁
22	CCC symmetric stretch	838	10.5	10.5	0.60	58S ₂₂ , 17S ₂₀ , 13S ₁₇	867	9.1	9.1	0.66	56S ₂₂ , 18S ₂₀ , 12S ₁₇
23	=CH ₂ wag	677	32.6	20.7	0.23	65S ₂₃ , 11S ₁₉	704	34.1	18.3	0.23	63S ₂₃ , 11S ₁₉
24	C=CC bend	540	18.0	18.2	0.36	28S ₂₄ , 23S ₂₇ , 20S ₂₅ , 11S ₂₂	569	16.8	17.2	0.37	25S ₂₄ , 25S ₂₅ , 21S ₂₇
25	CBr stretch	385	9.3	27.1	0.14	46S ₂₅ , 28S ₂₆	403	7.6	21.5	0.14	45S ₂₅ , 27S ₂₆ , 11S ₂₄
26	CCC bend	301	0.6	2.9	0.35	39S ₂₆ , 37S ₂₄	310	0.6	2.3	0.37	41S ₂₆ , 36S ₂₄
27	CBr bend	262	3.1	3.0	0.42	28S ₂₇ , 32S ₂₉ , 13S ₂₅ , 13S ₂₈	274	2.5	2.4	0.49	35S ₂₇ , 31S ₂₉ , 12S ₂₅
28	CH ₃ torsion	240	0.6	0.6	0.28	81S ₂₈	251	1.1	1.0	0.30	69S ₂₈ , 15S ₂₇
29	CBr bend	234	7.9	6.6	0.35	48S ₂₉ , 15S ₂₅ , 14S ₂₇	246	5.0	4.2	0.41	51S ₂₉ , 18S ₂₈
30	Asymmetric torsion	105	0.1	4.0	0.75	84S ₃₀	103	0.1	4.0	0.75	86S ₃₀

^a Calculated infrared intensities in km mol^{-1} .

^b Calculated Raman activities in $\text{\AA}^4 \text{amu}^{-1}$.

Table 5

Calculated wavenumbers (cm^{-1}) and potential energy distributions (PED) for the conformer with the methyl group eclipsing the double bond (ME) of 3-bromo-1-butene

Vib. no.	Description	BLYP/6-311 + + G(d,p)					B3LYP/6-311 + + G(d,p)				
		cm^{-1}	IR int ^a	Raman act. ^b	dp ratio	PED	cm^{-1}	IR int ^a	Raman act. ^b	dp ratio	PED
1	=CH ₂ antisymmetric stretch	3146	10.9	78.3	0.62	98S ₁	3226	8.8	70.8	0.63	98S ₁
2	=CH stretch	3075	4.0	171.1	0.15	69S ₂ , 28S ₃	3155	3.7	145.2	0.17	79S ₂ , 18S ₃
3	=CH ₂ symmetric stretch	3066	8.9	39.3	0.34	71S ₃ , 28S ₂	3143	5.8	49.1	0.24	81S ₃ , 18S ₂
4	CH ₃ antisymmetric stretch	3051	12.2	48.9	0.49	61S ₄ , 30S ₆	3127	11.2	47.1	0.49	62S ₄ , 31S ₆
5	CH stretch	3016	1.2	112.2	0.38	49S ₅ , 30S ₄ , 14S ₆	3091	0.3	107.3	0.38	64S ₅ , 24S ₄
6	CH ₃ antisymmetric stretch	3026	11.5	47.5	0.61	42S ₆ , 42S ₅	3102	12.9	47.7	0.65	51S ₆ , 28S ₅ , 13S ₄
7	CH ₃ symmetric stretch	2955	17.8	185.0	0.09	84S ₇ , 14S ₆	3031	16.2	161.6	0.07	89S ₇ , 10S ₆
8	C=C stretch	1626	3.6	119.0	0.19	67S ₈ , 18S ₁₁	1691	4.4	107.2	0.17	69S ₈ , 15S ₁₁
9	CH ₃ antisymmetric deformation	1465	3.3	8.5	0.50	78S ₉	1501	3.3	6.9	0.47	81S ₉
10	CH ₃ antisymmetric deformation	1452	7.2	7.7	0.47	80S ₁₀	1490	7.9	7.2	0.53	83S ₁₀
11	=CH ₂ deformation	1412	9.3	34.3	0.35	67S ₁₁ , 12S ₁₄	1449	10.9	28.0	0.38	68S ₁₁ , 11S ₁₄
12	CH ₃ symmetric deformation	1373	7.7	4.9	0.67	90S ₁₂	1413	8.3	4.4	0.59	86S ₁₂
13	CH bend	1334	3.8	7.9	0.46	67S ₁₃ , 12S ₁₆	1371	2.2	5.2	0.49	64S ₁₃ , 12S ₁₆
14	=CH bend, in-plane	1300	0.3	20.3	0.22	61S ₁₄ , 16S ₈ , 11S ₂₀	1333	0.3	18.2	0.23	62S ₁₄ , 16S ₈ , 11S ₂₀
15	CH bend	1157	20.3	41.4	0.35	45S ₁₅ , 19S ₁₈ , 15S ₁₆	1203	32.2	44.0	0.36	62S ₁₅ , 15S ₁₇
16	CCC antisymmetric stretch	1121	37.2	14.1	0.34	20S ₁₆ , 35S ₁₅ , 15S ₂₀	1161	28.7	7.4	0.41	27S ₁₆ , 21S ₁₅ , 16S ₂₀ , 10S ₁₃
17	CH ₃ rock	1064	12.9	2.4	0.58	51S ₁₇ , 11S ₁₆	1026	2.1	4.7	0.72	36S ₁₇ , 20S ₂₀
18	CH ₃ rock	998	3.3	4.9	0.74	23S ₁₈ , 32S ₁₉ , 13S ₂₃ , 11S ₂₀	1095	13.1	2.1	0.61	51S ₁₈
19	=CH bend, out-of-plane	992	7.9	2.6	0.72	46S ₁₉ , 14S ₁₈ , 11S ₂₀	1031	10.4	2.0	0.65	76S ₁₉ , 21S ₂₃
20	=CH ₂ rock	953	14.0	2.1	0.58	21S ₂₀ , 27S ₁₆ , 22S ₁₇	985	12.7	2.4	0.55	23S ₂₀ , 25S ₁₆ , 20S ₁₈
21	=CH ₂ twist	916	39.4	2.1	0.74	99S ₂₁	957	43.7	2.4	0.74	99S ₂₁
22	CCC symmetric stretch	818	8.3	14.3	0.67	75S ₂₂	850	7.0	12.0	0.70	72S ₂₂
23	=CH ₂ wag	677	30.2	19.6	0.32	59S ₂₃ , 14S ₂₇ , 13S ₁₉	705	31.1	18.0	0.33	60S ₂₃ , 15S ₂₇ , 12S ₁₉
24	C=CC bend	543	11.2	7.0	0.18	40S ₂₄ , 31S ₂₆	561	12.2	8.4	0.19	38S ₂₄ , 29S ₂₆ , 10S ₂₅
25	CBr stretch	441	12.5	29.4	0.23	43S ₂₅ , 33S ₂₇ , 14S ₂₃	469	9.5	23.4	0.23	43S ₂₅ , 26S ₂₇ , 15S ₂₃
26	CCC bend	287	0.9	5.6	0.21	47S ₂₆ , 38S ₂₄	299	1.1	5.1	0.20	44S ₂₆ , 37S ₂₄
27	CBr bend	255	3.9	6.9	0.20	26S ₂₇ , 34S ₂₈ , 21S ₂₅ , 18S ₂₉	269	2.2	3.5	0.22	25S ₂₇ , 45S ₂₈ , 13S ₂₅
28	CH ₃ torsion	275	2.6	5.5	0.23	64S ₂₈ , 17S ₂₅ , 11S ₂₉	289	2.6	5.0	0.22	53S ₂₈ , 19S ₂₅ , 13S ₂₉
29	CBr bend	234	5.9	4.5	0.44	54S ₂₉ , 11S ₂₅ , 11S ₂₇ , 10S ₃₀	245	4.3	3.1	0.53	54S ₂₉ , 11S ₂₇
30	Asymmetric torsion	102	0.1	2.9	0.75	92S ₃₀	105	0.2	2.9	0.75	92S ₃₀

^a Calculated infrared intensities in km mol^{-1} .^b Calculated Raman activities in $\text{\AA}^4 \text{amu}^{-1}$.

Table 6
Calculated wavenumbers (cm^{-1}) and potential energy distributions (PED) for the conformer with the bromine atom eclipsing the double bond (BrE) of 3-bromo-1-butene

Vib. no.	Description	BLYP/6-311 + + G(d,p)					B3LYP/6-311 + + G(d,p)				
		cm^{-1}	IR int ^a	Raman act. ^b	dp ratio	PED	cm^{-1}	IR int ^a	Raman act. ^b	dp ratio	PED
1	=CH ₂ antisymmetric stretch	3152	7.0	53.0	0.63	100S ₁	3232	5.6	49.7	0.63	100S ₁
2	=CH stretch	3022	21.5	179.9	0.42	80S ₂ , 11S ₆	3106	16.8	148.4	0.38	90S ₂
3	=CH ₂ symmetric stretch	3070	5.9	159.3	0.15	98S ₃	3146	4.2	151.3	0.15	97S ₃
4	CH ₃ antisymmetric stretch	3049	15.6	64.8	0.59	69S ₄ , 29S ₆	3126	14.3	60.0	0.58	67S ₄ , 29S ₆
5	CH stretch	2993	2.0	123.3	0.27	93S ₅	3073	1.4	116.3	0.29	91S ₅
6	CH ₃ antisymmetric stretch	3017	8.0	49.9	0.24	47S ₆ , 20S ₄ , 17S ₂ , 14S ₇	3095	10.9	45.6	0.58	57S ₆ , 24S ₄ , 11S ₇
7	CH ₃ symmetric stretch	2950	22.8	202.3	0.08	84S ₇ , 13S ₆	3026	21.2	180.9	0.06	89S ₇
8	C=C stretch	1643	15.3	44.5	0.09	72S ₈ , 13S ₁₁	1706	14.4	45.0	0.08	72S ₈ , 12S ₁₁
9	CH ₃ antisymmetric deformation	1459	3.4	6.9	0.75	70S ₉ , 21S ₁₀	1495	3.6	6.5	0.75	70S ₉ , 21S ₁₀
10	CH ₃ antisymmetric deformation	1450	6.6	10.1	0.70	69S ₁₀ , 19S ₉	1487	6.9	9.9	0.71	68S ₁₀ , 20S ₉
11	=CH ₂ deformation	1403	9.2	10.9	0.34	79S ₁₁	1441	10.6	9.7	0.36	79S ₁₁
12	CH ₃ symmetric deformation	1370	5.7	2.3	0.66	97S ₁₂	1410	6.7	1.8	0.60	97S ₁₂
13	CH bend	1285	4.6	11.0	0.40	76S ₁₃	1324	6.4	17.9	0.29	43S ₁₃ , 34S ₁₄
14	=CH bend, in-plane	1291	3.5	12.9	0.21	66S ₁₄ , 12S ₈ , 11S ₂₀	1328	1.4	4.5	0.23	35S ₁₄ , 33S ₁₃
15	CH bend	1191	43.0	15.4	0.35	69S ₁₅	1238	42.8	13.2	0.42	71S ₁₅
16	CCC antisymmetric stretch	947	9.4	3.3	0.67	38S ₁₆ , 21S ₁₈ , 19S ₁₇	981	9.9	2.7	0.64	34S ₁₆ , 21S ₁₈ , 21S ₁₇
17	CH ₃ rock	1044	1.2	3.6	0.62	20S ₁₇ , 33S ₁₆ , 12S ₂₂	1085	1.3	4.0	0.60	21S ₁₇ , 35S ₁₆ , 13S ₂₂
18	CH ₃ rock	1084	13.9	1.4	0.49	31S ₁₈ , 11S ₁₅ , 10S ₁₃	1119	14.3	1.3	0.56	31S ₁₈ , 11S ₁₅ , 10S ₁₃
19	=CH bend, out-of-plane	970	14.7	1.7	0.64	73S ₁₉ , 24S ₂₃	1009	12.7	1.6	0.65	75S ₁₉ , 23S ₂₃
20	=CH ₂ rock	1019	3.1	3.4	0.64	45S ₂₀ , 12S ₁₇ , 11S ₁₈	1049	3.6	2.9	0.61	46S ₂₀ , 13S ₁₈ , 10S ₁₇
21	=CH ₂ twist	921	35.7	1.7	0.71	99S ₂₁	962	40.1	2.0	0.73	97S ₂₁
22	CCC symmetric stretch	826	10.0	5.1	0.75	55S ₂₂ , 11S ₂₀ , 10S ₁₈	858	9.1	5.1	0.73	52S ₂₂ , 13S ₂₀ , 11S ₁₈
23	=CH ₂ wag	666	12.4	3.2	0.68	47S ₂₃ , 15S ₁₉	690	12.7	3.3	0.66	48S ₂₃ , 14S ₁₉
24	C=CC bend	567	14.2	13.6	0.09	25S ₂₄ , 21S ₂₇ , 16S ₂₅ , 11S ₂₂ , 10S ₂₃	590	14.6	13.3	0.10	23S ₂₄ , 19S ₂₇ , 18S ₂₅ , 12S ₂₂ , 11S ₂₃
25	CBr stretch	413	8.6	11.9	0.37	51S ₂₅ , 31S ₂₄	436	7.8	11.1	0.40	50S ₂₅ , 33S ₂₄
26	CCC bend	347	1.4	2.0	0.39	62S ₂₆ , 11S ₂₃	358	1.4	1.7	0.36	61S ₂₆ , 11S ₂₃
27	CBr bend	277	1.6	2.7	0.35	16S ₂₇ , 34S ₂₉ , 20S ₂₈ , 19S ₂₅	289	1.4	2.3	0.37	18S ₂₇ , 36S ₂₉ , 17S ₂₅ , 16S ₂₈
28	CH ₃ torsion	249	0.6	0.7	0.56	79S ₂₈ , 12S ₂₇	257	0.5	0.5	0.62	83S ₂₈ , 11S ₂₇
29	CBr bend	200	0.4	2.6	0.44	42S ₂₉ , 24S ₂₇ , 23S ₂₄	209	0.3	2.4	0.45	43S ₂₉ , 24S ₂₇ , 23S ₂₄
30	Asymmetric torsion	90	0.1	2.9	0.72	100S ₃₀	96	0.1	2.9	0.73	100S ₃₀

^a Calculated infrared intensities in km mol^{-1} .

^b Calculated Raman activities in $\text{\AA}^4 \text{amu}^{-1}$.

Table 7
Comparison of the conformational enthalpy differences and abundances obtained for 3-X-1-butenes

Molecule	Method	HE		ME		XE		Abundance (%)		
		Total energy	ΔH	Total energy	ΔH	Total energy	ΔH	HE	ME	XE
3-Bromo-1-butenes	BLYP/6-311++G(d,p)	-2730.725409	0	-2730.723810	4.20	-2730.721124	11.25	84	15	1
	B3LYP/6-311++G(d,p)	-2730.817307	0	-2730.815883	3.74	-2730.813636	9.64	81	18	2
3-Chloro-1-butenes	BLYP/6-311++G(d,p)	-616.785635	0	-616.783900	1.05	-616.782596	1.85	47	31	22
	B3LYP/6-311++G(d,p)	-616.895764	0	-616.894224	0.94	-616.893257	1.52	45	31	24
	IR temperature variance ^a		0		0.90(10)		2.36(44)	48(2)	33(1)	19(3)
3-Fluoro-1-butenes	BLYP/6-311++G(d,p)	-256.442042	0	-256.440235	4.74	-256.441154	2.33	65	10	25
	B3LYP/6-311++G(d,p)	-256.540285	0	-256.538737	4.06	-256.539923	0.95	53	10	36
	IR temperature variance ^b		0		3.49(6)		1.04(7)	53(1)	13(0)	35(1)

X=F, Cl and Br. Total energies in hartree, ΔH in kJ mol⁻¹.

^a Taken from Ref. [2].

^b Taken from Ref. [1].

same mode in the chlorine (vib. no=6) and fluorine (vib. no=7). The out-of-plane =CH bend was predicted to be present in the higher region of 980 cm⁻¹ than the same mode of chlorine and fluorine analogues (~600 cm⁻¹). For the heavy atom modes, the CBr stretches of three conformers were predicted at the ~400 cm⁻¹ region and the two CBr bends at the ~260 and 230 cm⁻¹ region.

3.3. Comparison of conformational stability of 3-halo-butenes

A review of the values of the conformational enthalpy differences obtained for 3-halo-1-butenes is summarized in Table 7. The values of the ΔH between the HE and ME varies from 3.74 to 4.31 kJ mol⁻¹ and those between the HE and BrE from 8.37 to 11.3 kJ mol⁻¹, depending on the choice of basis set. These ΔH values indicate that the most stable conformer of the molecule is the HE, the second and the third are the ME and the BrE, respectively. The ΔH between the HE and BrE of 3-bromo-1-butene is significantly larger than those of 3-fluoro-1-butene [1] and 3-chloro-1-butene [2]. This can explain the largest ΔH value is due to the largest size of the bromine atom eclipsing the methylene hydrogen.

Utilizing the ΔH values the abundance ratios of conformers in the gaseous phase at ambient temperature were calculated by Boltzmann distribution equation [14]

$$\frac{N_i}{N_j} = \exp(-\Delta H/RT),$$

where N_i is the number of the higher energy conformer, N_j is the number of the most stable conformer, ΔH is the enthalpy difference between the conformers, R is the gas constant and T is the absolute temperature. The estimated concentrations of the HE, ME and FE are about 83, 15 and 3%. Therefore the BrE conformer of 3-bromo-1-butene may not be easily detected in the spectral measurement because of insufficient abundance. But the ME conformer may be present with enough abundance in the fluid phases.

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