Thermochemistry of oxabicycloheptenes: enthalpy of formation, entropy and heat capacity

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ABSTRACT: Cyclohexene isomers with an epoxide ring (oxabicycloheptenes) are reportedly formed in atmospheric photochemical oxidation of aromatics. They may also be formed in higher temperature oxidation and oxygen-catalyzed pyrolysis of aromatics. Thermochemical properties, $\Delta H_{f(298)}^{\circ}$, S_{298}° and $C_p(T)$ ($10\,\mathrm{K} \leq T \leq 5000\,\mathrm{K}$) of five target oxabicycloheptenes were calculated using density functional methods. Structures for 7-oxabicyclo[4.1.0]hept-2-ene, 7-oxabicyclo[4.1.0]hept-3-ene, 7-oxabicyclo[3.1.1]hept-1-ene, 7-oxabicyclo[3.1.1]hept-2-ene and 7-oxabicyclo[2.2.1]hept-2-ene were calculated at the B3LYP/6–31g(d,p) level of theory. Enthalpies of formation were determined at the B3LYP/6–31G(d,p) calculation level using isodesmic and homodesmic working reactions with the $\Delta H^{\circ}_{\mathrm{rxn}}$ and known enthalpies of reference reactants in each of four different work reactions. Enthalpy values for the following bicyclic ether structures were also calculated for comparison of the calculation method with literature: 6-oxabicyclo[3.1.0]hexane, 7-oxabicyclo[4.1.0]heptane, 8-oxabicyclo[5.1.0]octane, 7-oxabicyclo[2.2.1]heptane, *endo*-2-methyl-7-oxabicyclo[2.2.1]heptane, *exo*-2-methyl-7-oxabicyclo[2.2.1]heptane and 7-oxabicyclo[4.1.0]hept-2,4-ene. Entropy (298 K) and heat capacity [$C_p(T)$] values along with Benson group additivity parameters for each ring system are reported. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: enthalpy of formation; entropy; heat capacity; oxabicycloheptenes; oxabicyclohexanes; oxabicycloheptanes

INTRODUCTION

Cyclic oxygenated hydrocarbons are important intermediates in chemical processes such as combustion, photochemical oxidation and biological degradation of hydrocarbons. Many biological molecules, including sugars, starches and nucleic acid segments, include cyclic ethers in addition to alcohol moieties. The initial breakdown products of cellulose and similar natural materials in pyrolysis and combustion are cyclic and bicyclic oxygenated hydrocarbons.[1] Reactions of alkyl radicals with molecular oxygen in combustion processes form peroxy species, which are reported to react further forming cyclic ethers[2] and hydroperoxides. Thermodynamic properties of these species are important parameters for use in modeling the formation and destruction reaction paths of these chemicals.

In this work, we utilized density functional molecular orbital calculations and homodesmic or isodesmic reactions to calculate the enthalpies of formation, entropies and heat capacities of five oxabicycloheptenes.

CALCULATIONS

Quantum mechanical calculations were carried out using the Gaussian 98 computational chemistry computer code.[3] The structural parameters were optimized at the B3LYP/6–31g(d,p) level of theory.[4] The harmonic vibration frequencies and zero-point vibrational energies were computed at the same level. B3LYP/6–31g(d,p) was chosen because it has been shown to provide accurate thermochemical parameters in a number of studies on oxygenated hydrocarbons.[5–10] B3LYP is also commonly used and it is reported to yield accurate geometry and reasonable energies[11,12] (enthalpies of formation) on oxygenated and monochlorooxy hydrocarbons.[13–16] The studies have shown that it is accurate when used with homodesmic or isodesmic working reactions, where the bonding environments are similar on both sides of the working reactions. A homodesmic reaction is a hypothetical reaction where the number and type of bonds (according to the state of hybridization) are

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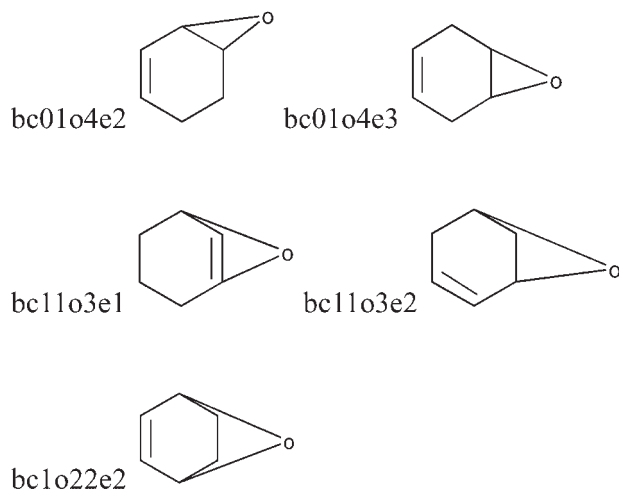
Scheme 1. Target bicyclic ethers and their structures and abbreviated nomenclature. 7-oxabicyclo[4.1.0]hept-2-ene = bc01o4e2; 7-oxabicyclo[4.1.0]hept-3-ene = bc01o4e3; 7-oxabicyclo[3.1.1]hept-1-ene = bc11o3e1; 7-oxabicyclo[3.1.1]hept-2-ene = bc11o3e2; 7-oxabicyclo[2.2.1]hept-2-ene = bc1o22e2

Scheme 2. Structures of reference compounds and abbreviated nomenclature. yc3h6o = oxetane; ycoc = ethylene oxide; cycoc = propylene oxide; yc4h8o = tetrahydrofuran; yccc = cyclopropane; ycccc = cyclobutane; yc5e = cyclopentene; yc6e = cyclohexene; y = cyclic

conserved on both sides of the reaction. An isodesmic reaction is one in which the number of bonds of each type are conserved on each side of the work reaction.

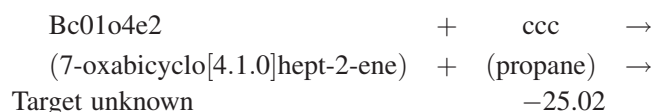The structures of five target molecules and an abbreviated nomenclature are presented in Scheme 1.

Enthalpies of formation [$\Delta H^\circ_{f(298)}$] were estimated using calculated energies, plus zero point vibration energy (ZPVE), plus thermal contributions (to 298 K) corresponding to the enthalpy of each species[17] in the work reaction. ΔH°_{rxn} was then calculated. We used the calculated ΔH°_{rxn} in the formula

$$\Delta H_{rxn(298)} = \Sigma H_{f\ products} - \Sigma H_{f\ reactants}$$
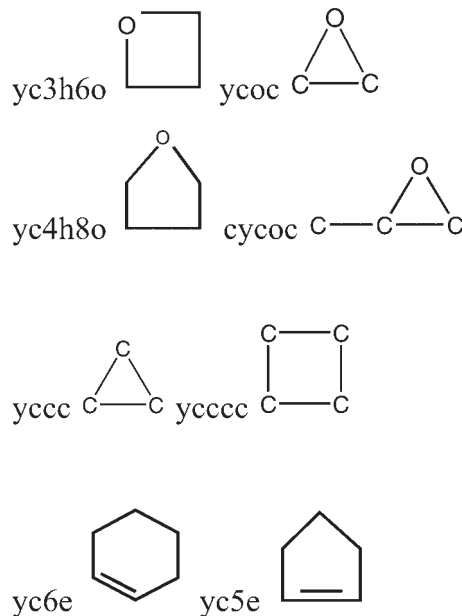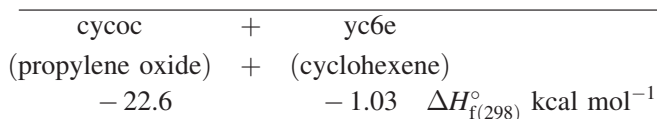
where the two products and one reactant are the three reference molecules, to find $\Delta H^\circ_{f(298)}$ of the target reactant. We used the evaluated literature thermodynamic properties for the three reference species.

The structures of the reference species used to find $\Delta H^\circ_{f(298)}$ for all the five target molecules and an abbreviated nomenclature are presented in Scheme 2.

As an example, the following equation was used to estimate $\Delta H^\circ_{f(298)}$ for 7-oxabicyclo[4.1.0]hept-2-ene.

target 7-oxabicyclo[4.1.0]hept-2-ene is obtained from Hess's law:

$$\begin{aligned}
\Delta H^\circ_{rxn,298} &= [(-193.0276825) + (-234.5125757) \\
&\quad - (-308.4935455) - (-119.0481883)] \times 627.51 \\
&= -22.63 + (-1.03) - \\
&\quad \Delta H^\circ_{f298}(\text{7-oxabicyclo[4.1.0]hept-2-ene}) + 25.02 \\
&\quad \Delta H^\circ_{f(298)}(\text{7-oxabicyclo[4.1.0]hept-2-ene}) \\
&= 0.43 \text{kcal mol}^{-1}
\end{aligned}$$

The methods of isodesmic or homodesmic work reactions rely on the similarity of bonding environment in the reactants and products that leads to cancellation of systematic errors in the density functional calculations. The zero point energies were scaled by 0.9806, as recommended by Scott and Radom[18] for B3LYP/6–31G(d,p) and thermal correction to 298.15 K.

Calculations were performed on each species in four work reactions for each oxabicycloheptene in this study. The consistency obtained across the different work

Bc01o4e2	+	ccc	→	cycoc	+	yc6e	
(7-oxabicyclo[4.1.0]hept-2-ene)	+	(propane)	→	(propylene oxide)	+	(cyclohexene)	
Target unknown		−25.02		− 22.6		− 1.03	$\Delta H^\circ_{f(298)}$ kcal mol^{-1}

Since enthalpies of formation of the three reference compounds are well established in the literature and ΔH°_{rxn} is calculated, the enthalpy of formation of the

reactions demonstrates precision and suggests reasonable accuracy. An analysis for estimation of error in the work reaction method was also developed.

Table 1. Optimized Geometry of Bc01o4e2[a]
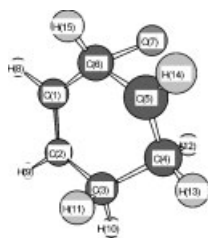
Definition[b]	Value (Å)	Definition[c]	Value (°)	Definition[d]	Value (°)
R(1,2)	1.337	A(2,1,6)	121.06	D(6,1,2,3)	−0.80
R(1,6)	1.487	A(2,1,8)	120.88	D(6,1,2,9)	178.06
R(1,8)	1.087	A(6,1,8)	118.05	D(8,1,2,3)	−179.72
R(2,3)	1.510	A(1,2,3)	122.94	D(8,1,2,9)	−0.86
R(2,9)	1.088	A(1,2,9)	119.74	D(2,1,6,5)	14.05
R(3,4)	1.543	A(3,2,9)	117.31	D(2,1,6,7)	81.87
R(3,10)	1.096	A(2,3,4)	113.22	D(2,1,6,15)	−138.57
R(3,11)	1.101	A(2,3,10)	109.80	D(8,1,6,5)	−167.00
R(4,5)	1.525	A(2,3,11)	108.62	D(8,1,6,7)	−99.18
R(4,12)	1.095	A(4,3,10)	109.46	D(8,1,6,15)	40.37
R(4,13)	1.095	A(4,3,11)	110.12	D(1,2,3,4)	−26.82
R(5,6)	1.472	A(10,3,11)	105.32	D(1,2,3,10)	−149.49
R(5,7)	1.438	A(3,4,5)	113.13	D(1,2,3,11)	95.83
R(5,14)	1.091	A(3,4,12)	109.40	D(9,2,3,4)	154.29
R(6,7)	1.448	A(3,4,13)	109.81	D(9,2,3,10)	31.62
R(6,15)	1.091	A(5,4,12)	107.17	D(9,2,3,11)	−83.06

[a] Geometry optimized at the B3LYP/6–31g(d,p) density functional calculation level.
[b] Bond length or the distance between two atoms of given number.
[c] Bond angle or the angle among three atoms of given number.
[d] Dihedral angle among the four atoms of given number.

RESULTS AND DISCUSSION

Geometry and vibrational frequencies

The optimized geometries at the B3LYP/6–31G(d,p) level for the five oxabicycloheptenes are illustrated in Tables 1–5. Harmonic vibrational frequencies and moments of inertia for the two cyclohexene oxirane isomers, two cyclohexene oxetane isomers and one cyclohexene oxolane isomer are given in Tables 6 and 7, respectively. Harmonic vibrational frequencies calculated at the B3LYP/6–31G(d,p) level of theory were scaled by 0.9806. Moments of inertia were optimized at the B3LYP/6–31G(d,p) level of theory. Bc11o3e1 (7-oxabicyclo [3.1.1] hept-1-ene) has an sp[2] carbon in both the oxetane and the cyclic hexene rings. This results in very high ring strain and increases the enthalpy of the molecule by 40 kcal mol^{-1} relative to other isomers in this study. The four-membered oxetane ring is effectively perpendicular to the five carbons of the cyclohexene ring.

Thermochemical properties

Total energies for the oxabicycloheptenes and all standard species in isodesmic reactions were calculated at the

B3LYP/6–31G(d,p) level (Table 8). ZPVEs and thermal corrections are also listed in Table 8. Scott and Radom reported r.m.s. errors of 0.1 kcal mol^{-1} for ZPVE, after scaling [0.9806 for B3LYP/6–31G(d,p) in their study on 39 molecules incorporating 1066 known vibrations]. They also reported r.m.s. errors of ca 0.01 kcal mol^{-1} for thermal correction from 0 to 298 K for this level of DFT[18] calculation.

The enthalpies of formation [$\Delta H^{\circ}_{\mathrm{f}(298)}$] were estimated using total energies and calculated $\Delta H^{\circ}_{\mathrm{rxn},298}$ for the listed reactions; the data for the reference species for the work reactions are given in Table 9. The reaction enthalpies and $\Delta H^{\circ}_{\mathrm{f}(298)}$s of the two cyclohexene oxirane isomers, two cyclohexene oxetane isomers and one cyclohexene oxolane isomer obtained from the use of the reaction schemes are given in Table 10. As noted above, four working reactions were used to determine the enthalpy of each bicyclic epoxide.

We performed additional computations using two reaction series to calculate the enthalpy of oxirane and compare the calculated value with data from the literature. These reactions are given below and show agreement with the recommended literature value of −12.58 kcal mol^{-1} for $\Delta H^{\circ}_{\mathrm{f}(298)}$.
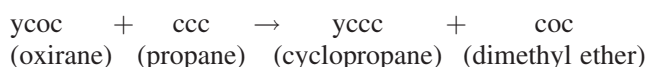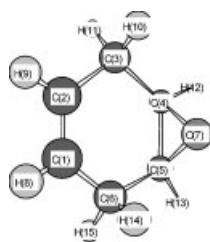
ycoc + ccc → yccc + coc
(oxirane) (propane) (cyclopropane) (dimethyl ether)

Table 2. Optimized geometry of Bc01o4e3[a]

Definition[b]	Value (Å)	Definition[c]	Value (°)	Definition[d]	Value (°)
R(1,2)	1.334	A(2,1,6)	124.38	D(6,1,2,3)	−0.01
R(1,6)	1.506	A(2,1,8)	119.33	D(6,1,2,9)	179.61
R(1,8)	1.088	A(6,1,8)	116.28	D(8,1,2,3)	−179.62
R(2,3)	1.506	A(1,2,3)	124.39	D(8,1,2,9)	0.00
R(2,9)	1.088	A(1,2,9)	119.33	D(2,1,6,5)	9.44
R(3,4)	1.513	A(3,2,9)	116.28	D(2,1,6,14)	132.18
R(3,10)	1.099	A(2,3,4)	113.84	D(2,1,6,15)	−112.22
R(3,11)	1.101	A(2,3,10)	110.10	D(8,1,6,5)	−170.94
R(4,5)	1.473	A(2,3,11)	109.69	D(8,1,6,14)	−48.20
R(4,7)	1.436	A(4,3,10)	109.00	D(8,1,6,15)	67.41
R(4,12)	1.092	A(4,3,11)	108.41	D(1,2,3,4)	−9.41
R(5,6)	1.513	A(10,3,11)	105.44	D(1,2,3,10)	−132.15
R(5,7)	1.436	A(3,4,5)	121.09	D(1,2,3,11)	112.26
R(5,13)	1.092	A(3,4,7)	116.31	D(9,2,3,4)	170.96
R(6,14)	1.099	A(3,4,12)	115.41	D(9,2,3,10)	48.22
R(6,15)	1.101	A(5,4,12)	118.44	D(9,2,3,11)	−67.38

[a] Geometry optimized at the B3LYP/6–31g(d,p) density functional calculation level.
[b] Bond length or the distance between two atoms of given number.
[c] Bond angle or the angle among three atoms of given number.
[d] Dihedral angle among the four atoms of given number.

Table 3. Optimized geometry of Bc11o3e1[a]
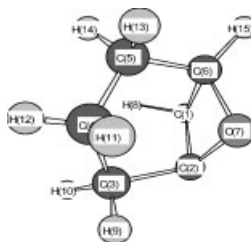
Definition[b]	Value (Å)	Definition[c]	Value (°)	Definition[d]	Value (°)
R(1,2)	1.359	A(2,1,6)	82.61	D(6,1,2,3)	99.39
R(1,6)	1.516	A(2,1,8)	129.44	D(6,1,2,7)	−21.50
R(1,8)	1.083	A(6,1,8)	131.47	D(8,1,2,3)	−39.89
R(2,3)	1.483	A(1,2,3)	123.74	D(8,1,2,7)	−160.78
R(2,7)	1.417	A(1,2,7)	97.80	D(2,1,6,5)	−81.57
R(3,4)	1.611	A(3,2,7)	110.34	D(2,1,6,7)	20.58
R(3,9)	1.094	A(2,3,4)	99.07	D(2,1,6,15)	141.70
R(3,10)	1.093	A(2,3,9)	115.29	D(8,1,6,5)	56.18
R(4,5)	1.568	A(2,3,10)	111.82	D(8,1,6,7)	158.33
R(4,11)	1.091	A(4,3,9)	109.68	D(8,1,6,15)	−80.55
R(4,12)	1.094	A(4,3,10)	111.60	D(1,2,3,4)	−63.79
R(5,6)	1.577	A(9,3,10)	109.07	D(1,2,3,9)	179.29
R(5,13)	1.096	A(3,4,5)	115.95	D(1,2,3,10)	53.95
R(5,14)	1.096	A(3,4,11)	107.02	D(7,2,3,4)	51.14
R(6,7)	1.464	A(3,4,12)	108.33	D(7,2,3,9)	−65.77
R(6,15)	1.097	A(5,4,11)	108.22	D(7,2,3,10)	168.88

[a] Geometry optimized at the B3LYP/6–31g(d,p) density functional calculation level.
[b] Bond length or the distance between two atoms of given number.
[c] Bond angle or the angle among three atoms of given number.
[d] Dihedral angle among the four atoms of given number.
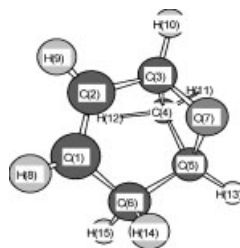
Table 4. Optimized geometry of Bc11o3e2[a]

Definition[b]	Value (Å)	Definition[c]	Value (°)	Definition[d]	Value (°)
R(1,2)	1.336	A(2,1,6)	118.61	D(6,1,2,3)	−0.01
R(1,6)	1.517	A(2,1,8)	122.33	D(6,1,2,9)	179.53
R(1,8)	1.087	A(6,1,8)	119.05	D(8,1,2,3)	179.09
R(2,3)	1.517	A(1,2,3)	115.96	D(8,1,2,9)	−1.37
R(2,9)	1.086	A(1,2,9)	123.12	D(2,1,6,5)	−1.81
R(3,4)	1.548	A(3,2,9)	120.91	D(2,1,6,14)	118.69
R(3,7)	1.468	A(2,3,4)	109.43	D(2,1,6,15)	−123.61
R(3,10)	1.093	A(2,3,7)	108.39	D(8,1,6,5)	179.06
R(4,5)	1.545	A(2,3,10)	114.70	D(8,1,6,14)	−60.44
R(4,11)	1.092	A(4,3,7)	88.77	D(8,1,6,15)	57.26
R(4,12)	1.093	A(4,3,10)	120.07	D(1,2,3,4)	50.47
R(5,6)	1.538	A(7,3,10)	112.25	D(1,2,3,7)	−44.89
R(5,7)	1.462	A(3,4,5)	81.52	D(1,2,3,10)	−171.19
R(5,13)	1.095	A(3,4,11)	112.25	D(9,2,3,4)	−129.09
R(6,14)	1.098	A(3,4,12)	118.37	D(9,2,3,7)	135.56
R(6,15)	1.099	A(5,4,11)	111.26	D(9,2,3,10)	9.26

[a] Geometry optimized at the B3LYP/6–31g(d,p) density functional calculation level.
[b] Bond length or the distance between two atoms of given number.
[c] Bond angle or the angle among three atoms of given number.
[d] Dihedral angle among the four atoms of given number.

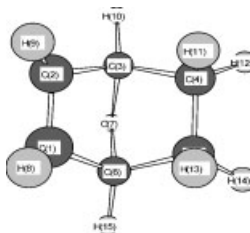**Table 5.** Optimized geometry of Bc1o22e2[a]

Definition[b]	Value (Å)	Definition[c]	Value (°)	Definition[d]	Value (°)
R(1,2)	1.3373	A(2,1,6)	121.0583	D(6,1,2,3)	−0.8038
R(1,6)	1.4874	A(2,1,8)	120.8828	D(6,1,2,9)	178.0592
R(1,8)	1.0873	A(6,1,8)	118.0503	D(8,1,2,3)	−179.7183
R(2,3)	1.5102	A(1,2,3)	122.9426	D(8,1,2,9)	−0.8554
R(2,9)	1.0883	A(1,2,9)	119.7376	D(2,1,6,5)	14.0537
R(3,4)	1.5428	A(3,2,9)	117.3106	D(2,1,6,7)	81.8716
R(3,10)	1.096	A(2,3,4)	113.2184	D(2,1,6,15)	−138.5702
R(3,11)	1.1007	A(2,3,10)	109.8014	D(8,1,6,5)	−167.0019
R(4,5)	1.5253	A(2,3,11)	108.6189	D(8,1,6,7)	−99.1839
R(4,12)	1.0952	A(4,3,10)	109.4602	D(8,1,6,15)	40.3743
R(4,13)	1.0953	A(4,3,11)	110.1176	D(1,2,3,4)	−26.8202
R(5,6)	1.472	A(10,3,11)	105.3218	D(1,2,3,10)	−149.4868
R(5,7)	1.4377	A(3,4,5)	113.1305	D(1,2,3,11)	95.8264
R(5,14)	1.0909	A(3,4,12)	109.3972	D(9,2,3,4)	154.2909
R(6,7)	1.448	A(3,4,13)	109.8065	D(9,2,3,10)	31.6244
R(6,15)	1.0911	A(5,4,12)	107.1688	D(9,2,3,11)	−83.0624
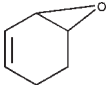
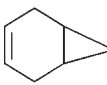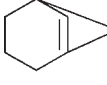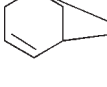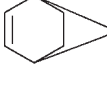[a] Geometry optimized at the B3LYP/6–31g(d,p) density functional calculation level.
[b] Bond length or the distance between two atoms of given number.
[c] Bond angle or the angle among three atoms of given number.
[d] Dihedral angle among the four atoms of given number.

Table 6. Vibrational frequencies(cm^{-1})[a]

			Sym = 1					OI = 2		
	117,	248,	396,	480,	502,	539,	715,	758,	793,	827
	873,	944,	972,	975,	996,	1049,	1062,	1090,	1146,	1199
	1216,	1275,	1290,	1355,	1359,	1402,	1430,	1473,	1488,	1498
bc01o4e2	1721,	3009,	3054,	3071,	3099,	3113,	3124,	3160,	3185	
			Sym = 2					OI = 1		
	127,	320,	361,	388,	535,	583,	672,	774,	801,	889
	908,	924,	955,	973,	1004,	1044,	1053,	1090,	1148,	1212
	1237,	1253,	1298,	1369,	1386,	1393,	1437,	1478,	1479,	1494
bc01o4e3	1747,	3009,	3010,	3038,	3038,	3102,	3114,	3155,	3177,	
			Sym = 1					OI = 2		
	137,	322,	389,	498,	603,	673,	721,	762,	806,	836
	855,	885,	915,	948,	972,	1036,	1044,	1113,	1181,	1198
	1201,	1218,	1269,	1292,	1313,	1337,	1352,	1491,	1508,	1520
bc11o3e1	1595,	3046,	3057,	3069,	3081,	3091,	3120,	3141,	3230,	
			Sym = 1					OI = 3		
	277,	348,	442,	498,	566,	680,	725,	827,	857,	874
	912,	934,	956,	966,	971,	1010,	1068,	1105,	1110,	1172
	1180,	1233,	1258,	1318,	1331,	1348,	1375,	1406,	1477,	1500
bc11o3e2	1706,	3023,	3055,	3077,	3086,	3105,	3145,	3171,	3198,	
			Sym = 2					OI = 1		
	249,	383,	481,	593,	709,	714,	795,	835,	841,	852
	889,	918,	931,	939,	954,	993,	1051,	1053,	1116,	1145
	1207,	1231,	1249,	1281,	1295,	1330,	1351,	1353,	1495,	1517
bc1o22e2	1654,	3073,	3083,	3119,	3134,	3140,	3144,	3221,	3245	

[a] Frequencies were calculated at the B3LYP/6–31G(d,p) level of theory scaled by 0.9806.

with $\Delta H^{\circ}_{\mathrm{f(298)}}$ (oxirane) $= -12.76\,\mathrm{kcal\,mol}^{-1}$.

ycoc   +   cccc   →   ycccc   +   coc
(oxirane) (butane) (cyclobutane) (dimethyl ether)

with $\Delta H^{\circ}_{\mathrm{f(298)}}$ (oxirane) $= -11.54\,\mathrm{kcal\,mol}^{-1}$.

The average of the values from the working reactions (Table 10) are recommended for $\Delta H^{\circ}_{\mathrm{f(298)}}$ of the target oxabicycloheptenes. The enthalpy values of all the bicyclic ethers with one double bond in the rings where no sp^2 carbon in bonded to the oxygen, are all between 4.8 and −4.1 kcal mol^{-1}. The one ring system with the double bond coupled (bonded) to the oxygen of ether link (bridge carbon in 7-oxybicyclo[3.1.1]hept-1-ene) shows exceptionally high ring strain with an enthalpy value of 42.7 kcal mol^{-1}, some 38–46 kcal mol^{-1} higher than for other cyclic of the ethers in this grouping. This high strain

Table 7. Moments of inertia (amu bohr^2)[a]

Species	I_a	I_b	I_c
bc01o4e2	411.99406	575.37153	873.56261
bc01o4e3	443.39154	535.00892	836.07078
bc11o3e1	431.54707	503.22726	649.54535
bc11o3e2	421.85614	515.55804	664.6773
bc1o22e2	432.76274	513.03371	583.59073

[a] Optimized at the B3LYP/6–31G(d,p) level of theory.

Table 8. Total energies at 298 K[a]

Species[b]	B3LYP/6–31[c]	ZPVE[d]	H_{298}–H_0^e
cc	−79.76078128	46.11145664	2.80873476
ccc	−119.0481883	63.82145099	3.43310721
cccc	−158.3354666	81.4465288	4.20055194
yc3h6o	−193.0227512	53.57548615	3.18900582
coc	−154.9493517	49.17398556	3.2944275
ycoc	−153.7315125	35.3547628	2.56965345
cycoc	−193.0276825	52.69801658	3.35341344
yc4h8o	−232.339739	71.94265955	3.70293651
yccc	−117.8199515	50.13452553	2.70519561
ycccc	−157.1101309	68.06973284	2.82693255
bc01o4e2	−308.4935455	78.53291139	4.21937724
bc01o4e3	−308.5003722	78.49660655	4.1854917
bc11o3e1	−308.4257759	78.2806235	4.06814733
bc11o3e2	−308.4862285	78.93780268	3.8529114
bc1o22e2	−308.5009114	79.31684984	3.75501984
yc6e	−234.5125757	90.14615349	4.04681199
yc5e	−195.2185527	71.9518896	3.50903592

[a] All calculations based on B3LYP/6–31g(d,p)-optimized structures.
[b] cc = Ethane, ccc = propane, cccc = butane, coc = dimethyl ether.
[c] Total energies calculated at the B3LYP/6–31g(d,p) level at 298 K in hartrees; 1 hartree = 627.51 kcal mol^{-1}.
[d] Zero point vibrational energy scaled by 0.9806.
[e] Thermal correction.

is also reflected in the enthalpy component of the bc11o3e1 ring group below. The dihedral angles in Table 3 illustrate the near perpendicular nature of the two ring components at this ether–carbon double bond juncture.

The error limits are the standard deviations obtained in taking the standard deviation from the work reaction method (see below), the average values from the working reactions plus the sum of uncertainties from 1) the three standard species, 2) the ZPVE calculations and 3) the thermal energies. The literature recommended uncertainties of the standard species are included in Table 9 and error limit analysis from the work reaction calculation method is discussed below.

We calculated enthalpy values for seven oxabicyclo ring systems where there are known or estimated literature enthalpy values for comparison in order to test or validate our B3LYP/6–31G(d,p) work reaction method for these large bicyclic ether ring systems. These added bicyclic ether ring systems are illustrated in Scheme 3 and listed in Table 11.

The agreement illustrated in Table 11 is judged very good for comparison with values where difficult experiments for the enthalpy data are required. The average deviation is $1.48\,kcal\,mol^{-1}$, including one largest deviation at $3.2\,kcal\,mol^{-1}$.

The accuracy of the $\Delta H^{\circ}_{f(298)}$ obtained from the use of computational chemistry is controlled by several factors:

Table 9. Enthalpies of formation for reference species

Species	ΔH°_{f298} (kcal mol^{-1})	Uncertainty (kcal mol^{-1})	Source (Ref. No.)
cc	−20.24	± 0.12	19
ccc	−25.02	± 0.12	20
cccc	−30.37	± 0.16	21
yc3h6o	−19.24	± 0.14	20
coc	−43.99	± 0.12	22
ycoc	−12.58	± 0.15	23
cycoc	−22.63	± 0.15	24
yc4h8o	−44.03	± 0.17	25
yccc	12.74	± 0.14	20
ycccc	6.79	± 0.14	20
yc5e	8.1	± 0.33	20
yc6e	−1.03	± 0.23	26

(1) the choice of the working chemical reactions used to cancel calculation errors; (2) the level of sophistication (method + basis set) applied to calculate the electronic energy; (3) the uncertainty of the ZPVEs and thermal corrections; (4) the accuracy and error tolerance of the $\Delta H^{\circ}_{f(298)}$ of the three reference compounds.

We also performed an error analysis on several known, but smaller ether, monocyclic ring systems to develop an estimate standard deviation of the $\Delta H_{rxn(298)}$ work reaction calculation method. These data are given in Table 12 and show an average deviation of $0.78\,kcal\,mol^{-1}$ at 1 standard deviation.

Table 10. Reaction enthalpies at 298 K and calculated enthalpies of formation[a,b]

Compound	Work reactions						B3LYP/6–31G(d,p)			
							ΔH°_{rxn}	ΔH°_{f298}	$\Delta H^{\circ}_{f298\ avg}$	Error limit
7-Oxabicyclo[4.1.0]hept-2-ene										
bc01o4e2	+	cc	→	ycoc	+	yc6e	6.43	0.21		
bc01o4e2	+	ccc	→	cycoc	+	yc6e	0.93	0.43		
bc01o4e2	+	ccc	→	yc3h6o	+	yc6e	4.02	0.73		
bc01o4e2	+	ccc	→	yc4h8o	+	yc5e	−10.39	−0.52	0.21	± 1.3
7-Oxabicyclo[4.1.0]hept-3-ene										
bc01o4e3	+	cc	→	ycoc	+	yc6e	10.71	−4.08		
bc01o4e3	+	ccc	→	cycoc	+	yc6e	5.21	−3.85		
bc01o4e3	+	ccc	→	yc3h6o	+	yc6e	8.30	−3.55		
bc01o4e3	+	ccc	→	yc4h8o	+	yc5e	−6.11	−4.80	−4.07	± 1.3
7-Oxabicyclo[3.1.1]hept-1-ene										
bc11o3e1	+	cc	→	ycoc	+	yc6e	−36.10	42.73		
bc11o3e1	+	ccc	→	cycoc	+	yc6e	−41.60	42.96		
bc11o3e1	+	ccc	→	yc3h6o	+	yc6e	−38.51	43.25		
bc11o3e1	+	ccc	→	yc4h8o	+	yc5e	−52.92	42.01	42.74	± 1.3
7-Oxabicyclo[3.1.1]hept-2-ene										
bc11o3e2	+	cc	→	ycoc	+	yc6e	1.83	4.80		
bc11o3e2	+	ccc	→	cycoc	+	yc6e	−3.67	5.03		
bc11o3e2	+	ccc	→	yc3h6o	+	yc6e	−0.57	5.32		
bc11o3e2	+	ccc	→	yc4h8o	+	yc5e	−14.98	4.07	4.81	± 1.3
7-Oxabicyclo[2.2.1]hept-2-ene										
bc1o22e2	+	cc	→	ycoc	+	yc6e	11.05	−4.42		
bc1o22e2	+	ccc	→	cycoc	+	yc6e	5.55	−4.19		
bc1o22e2	+	ccc	→	yc3h6o	+	yc6e	8.64	−3.89		
bc1o22e2	+	ccc	→	yc4h8o	+	yc5e	−5.77	−5.14	−4.41	± 1.3

[a] Reaction enthalpies include thermal correction and zero-point energy.
[b] Units in kcal mol^{-1}. Error is the sum of error in uncertainty for each species in work reaction (see uncertainty in Table 9) plus average absolute work reaction error (0.78 from Table 12).
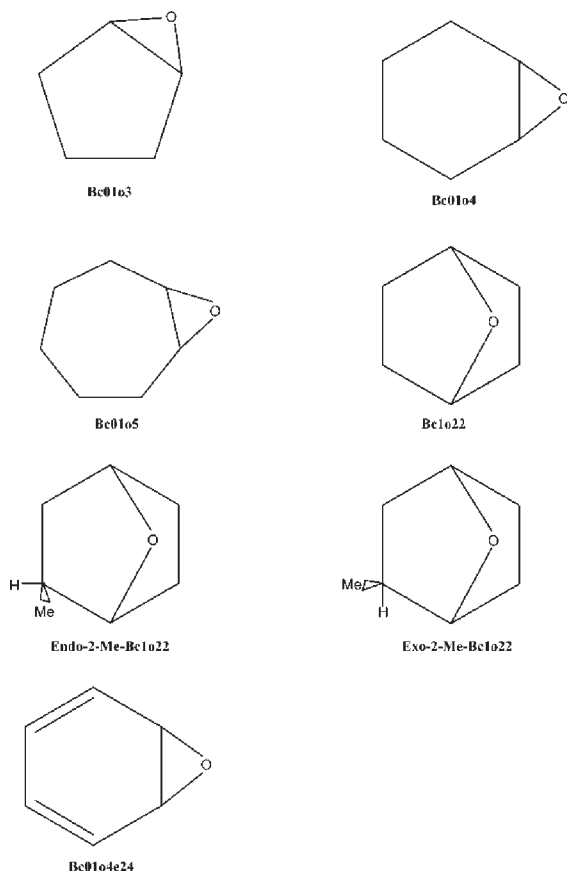
Scheme 3. Bicyclic ethers calculated for comparison with literature values for method validation and their abbreviated nomenclature (≡equivalent abbreviated name). 6-Oxabicyclo[3.1.0]hexane ≡ bc01o3; 7-oxabicyclo [4.1.0] heptane ≡ bc01o4; 8-oxabicyclo[5.1.0]octane ≡ bc01o5; 7-oxabicyclo[2.2.1]heptane ≡ bc1o22; *endo*-2-methyl-7-oxabicyclo[2.2.1] heptane ≡ *endo*-2-Me-bc1o22; *exo*- 2-methyl-7-oxabicyclo[2.2.1] heptane ≡ *exo*-2-Me-bc1o22; 7-oxabicyclo [4.1.0]hept-2,4-ene ≡ bc01o4e24

Entropy and heat capacity data

Entropy and heat capacity contributions as a function of temperature were determined from the calculated structures, moments of inertia, vibration frequencies and the known mass of each molecule. The calculations uses standard equations from statistical mechanics for the contributions of translation, external rotation and vibrations. Contributions to S_{298}° and $C_p(T)$ from translation, vibrations and external rotation were calculated using the SMCPS program.[31] This program utilizes the rigid rotor–harmonic oscillator approximation from the frequencies along with moments of inertia from the optimized B3LYP/6–31G(d,p) structures. Contributions from electronic degeneracy and unpaired electron spin are not needed for these stable molecules. Corrections for symmetry [–Rln(symmetry)] and optical isomers [Rln(OI)] are also included (Table 13).

Entropy data are needed in addition to enthalpy values in order to calculate Gibbs energy and equilibrium constants. Heat capacity data as a function of temperature are needed to calculate entropy (S_{298}°) and enthalpy as functions of temperature for the Gibbs energy and equilibrium values (T). Entropy and heat capacity [$C_p(T)$] calculation results from the B3LYP/6–31g(d,p) determined geometries and harmonic frequencies are summarized in Table 13. There are no internal rotors in these molecules, hence there needs to be no correction for assumed torsion frequencies.

Group values for use in the group additivity method for estimation of thermochemical properties

Group additivity[32] is a straightforward and reasonably accurate calculation method to estimate thermodynamic properties of hydrocarbons and oxygenated

Table 11. Comparison of additional calculated enthalpies of formation at 298 K with literature

Compound	Species	ΔH_{f298}° Literature (Ref.)[a]	ΔH_{f298}° Calc[b]	$\mid \Delta \mid$[f]
6-Oxabicyclo[3.1.0]hexane	bc01o3	−23.2 ± 1.7 (27)	−22.41	0.8
7-Oxabicyclo[4.1.0]heptane	bc01o4	−30.00 ± 0.26 (27)	−30.91	0.9
8-Oxabicyclo[5.1.0]octane	bc01o5	−36.40 ± 0.74 (27)	−33.16	3.2
7-Oxabicyclo[2.2.1]heptane	bc1o22	−43.40 ± 0.48 (28,29)[c]	−41.10	2.3
endo-2-Methyl-7-oxabicyclo[2.2.1]heptane	*endo*-2-Me-bc1o22	−48.63 ± 0.51 (28,29)[d]	−46.50	2.1
exo-2-Methyl-7-oxabicyclo[2.2.1]heptane	*exo*-2-Me-bc1o22	−49.48 ± 0.53 (28,29)[d]	−49.29	0.19
7-Oxabicyclo[4.1.0]hept-2,4-ene	bc01o4e24	20.7 (30)[e]	19.87	0.9

[a] Literature value of the species (kcal mol^{-1}) and reference in parenthesis.
[b] B3LYP/6–31g(d,p) plus working reactions in kcal mol^{-1}.
[c] Calculated from ΔH_{f298}°(liq) and the estimated ΔH(vap). ΔH(vap) was estimated from the ΔH(vap) of cyclopentenyl methyl ether in the temperature range 274–3 K with the mean temperature 298.
[d] Calculated ΔH_{f298}°(liq) and the estimated ΔH(vap). ΔH(vap) was estimated by adding the difference of the ΔH(vap) of cycloheptanone[29] at mean temperature 298 K and cyclohexanone[29] at mean temperature 298 K to the ΔH(vap) of cyclopentenyl methyl ether[29] at 298 K.
[e] Reported as in an aqueous phase at 0.1 M.
[f] Difference calculated versus literature, absolute value.

Table 12. Estimation of error from the work reaction component of the calculation method (Units: kcal mol^{-1} at 298 K)[a]

Reaction series						$\Delta H^{\circ}_{rxn\ calculated}$	$\Delta H^{\circ}_{rxn\ Literature}$	$|\Delta|$[b]
ycoc	+	ccc	→	coc	+	yccc	6.52	6.35	0.17
ycoc	+	cccc	→	coc	+	ycccc	4.70	5.75	1.05
yc3h6o	+	cc	→	ycoc	+	ccc	2.40	1.88	0.52
yc3h6o	+	ccc	→	ycoc	+	cccc	2.49	1.31	1.18
yc4h8o	+	cc	→	yc3h6o	+	ccc	18.56	20.01	1.45
yc4h8o	+	ccc	→	yc3h6o	+	cccc	18.64	19.44	0.80
yc4h8o	+	cc	→	ycoc	+	cccc	21.05	21.32	0.27
1 SD	± 0.996						Absolute average deviation	0.78[c]

[a] Reaction enthalpies include thermal correction and zero point energy determined at the B3LYP/6–31G(d,p) level of calculation.
[b] Difference literature – calculated, absolute value.
[c] The absolute average deviation is selected for reporting the error from the work reaction component. This includes error from the work reaction, the zero point vibration energies and the thermal energies; as all molecules, target and standards, are calculated at 298 K which includes the ZPVE and thermal energy in the calculation.

hydrocarbons;[33] it is particularly useful for application to larger molecules and in codes or databases for estimated thermochemical properties in reaction mechanism generation. In this work, we estimated five bicyclic oxy-hydrocarbon ring groups by using the thermodynamic property data developed in this study, plus the alkyl-hydrocarbon and oxy-hydrocarbon groups in the literature. The five bicyclic oxy-hydrocarbon groups are listed in Table 14, along with standard hydrocarbon and oxy-hydrocarbon groups used.

As an example, group parameters for $\Delta H^{\circ}_{f(298)}$, S°_{298} and $C_{p}(T)$ of 7-oxabicyclo [4.1.0]hept-2-ene (Bc01o4e2) were calculated on the basis of Table 15.

The group additivity method provides an accurate method to estimate thermochemical properties for cyclic molecules with the frame(s) as those in this study, but with a wide range of varied substituents.

The group values for Bc01o4e3, Bc11o3e1, Bc11o3e2 and Bc1o22e2 were estimated in the same manner. The group values are given in Table 14.

Table 13. Ideal gas-phase thermodynamic property vs temperature for the oxabicyclic heptanes[a]

Species symmetry (σ) [OI][b] (K)	bc01o4e2 (1)[c] [2]		bc01o4e3 (2) [1]		bc11o3e1 (1) [2]		bc11o3e2 (1) [3]		bc1o22e2 (2) [1]	
	$C_{p}(T)$	$S^{\circ}(T)$[d]	$C_{p}(T)$	$S^{\circ}(T)$[d]	$C_{p}(T)$	$S^{\circ}(T)$[d]	$C_{p}(T)$	$S^{\circ}(T)$[d]	$C_{p}(T)$	$S^{\circ}(T)$[d]
10.00	7.95	40.78	7.95	38.02	7.95	40.43	7.95	41.27	7.95	37.60
25.00	8.05	48.08	8.01	45.32	7.99	47.70	7.95	48.55	7.95	44.88
50.00	8.86	53.90	8.69	51.06	8.58	53.40	8.00	54.07	8.03	50.41
100.00	10.73	60.60	10.52	57.61	10.18	59.82	9.17	59.98	9.09	56.24
150.00	13.19	65.40	13.10	62.34	12.45	64.35	11.56	63.02	11.11	60.27
200.00	16.39	69.62	16.32	66.54	15.66	68.35	14.87	67.87	14.23	63.87
250.00	20.26	73.69	20.18	70.59	19.70	72.27	18.96	71.53	18.37	67.48
298.00	24.37	77.59	24.26	74.48	24.02	76.09	23.32	75.23	22.86	71.09
300.00	24.55	77.77	24.43	74.65	24.20	76.27	23.51	75.39	23.06	71.24
400.00	33.15	86.03	33.01	82.87	33.15	84.48	32.60	83.43	32.41	79.19
500.00	40.69	94.27	40.55	91.08	40.88	92.75	40.44	91.68	40.41	87.32
600.00	46.89	102.27	46.78	99.06	47.16	100.79	46.81	99.55	46.84	95.29
800.00	56.18	117.15	56.12	113.90	56.44	115.73	56.21	114.41	56.23	110.16
1000.00	62.70	130.42	62.69	127.19	62.92	129.08	62.75	127.72	62.73	123.46
1500.00	72.40	157.97	72.43	154.73	72.52	156.78	72.43	155.27	72.37	151.00
2000.00	77.24	179.56	77.27	176.33	77.31	178.31	77.26	176.87	77.20	172.58
2500.00	79.89	197.12	79.91	193.91	79.94	195.89	79.90	194.45	79.85	190.14
3000.00	81.46	211.87	81.48	208.65	81.49	210.63	81.47	209.19	81.43	204.87
3500.00	82.46	224.52	82.47	221.31	82.48	223.26	82.46	221.84	82.43	217.53
4000.00	83.13	235.59	83.14	232.38	83.15	233.82	83.13	232.92	83.11	228.59
4500.00	83.60	245.42	83.61	242.22	83.61	244.20	83.60	242.75	83.58	238.43
5000.00	83.94	254.28	83.95	251.06	83.95	253.05	83.94	251.59	83.92	247.26

[a] Thermodynamic properties are referred to the standard state of an ideal gas at 1 atm.
[d] S°_{298} and $C_{p}(T)$ in cal mol^{-1}.
[c] Symmetry number is taken into account [$-R\ln$(symmetry number, σ)].
[b] OI, No. of optical isomers – symmetry correction $+ R\ln$(OI).

Table 14. Group values[a]

Group[b]	ΔH°_{f298}	S°_{298}	$C_p(T)$						
			300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
Non-cyclic groups (known)									
CD/C/H[c]	8.59	7.97	4.16	5.03	5.81	6.50	7.65	8.45	9.62
C/C/CD/H/O[d]	−6.00	−11.10	4.47	6.82	8.45	9.17	10.24	10.80	11.02
O/C2[c]	−23.20	8.68	3.40	3.70	3.70	3.80	4.40	4.60	4.80
C/C2/H/O[c]	−7.20	−11.00	4.80	6.64	8.10	8.73	9.81	10.40	11.51
C/C2/H2[c]	−4.93	9.42	5.50	6.95	8.25	9.35	11.07	12.34	14.20
C/C/CD/H2[c]	−4.76	9.80	5.12	6.86	8.32	9.49	11.22	12.48	14.36
C/CD/C/H/O[d]	−6.00	−11.10	4.47	6.82	8.45	9.17	10.24	10.80	11.02
O/C/CD[d]	−29.70	5.44	4.04	4.73	4.99	5.04	4.97	4.81	4.49
CD/C/O[e]	8.20	−12.32	3.59	4.56	5.04	5.30	5.84	6.07	6.16
Bicyclic groups *(developed in this study)*									
Bc01o4e2	29.12	54.51	−7.06	−7.88	−7.75	−6.65	−5.86	−4.82	−2.73
Bc01o4e3	25.87	53.64	−7.13	−7.75	−7.61	−6.46	−5.64	−4.57	−3.35
Bc11o3e1	76.27	56.12	−8.18	−8.75	−8.23	−7.04	−5.62	−4.37	−1.53
Bc11o3e2	33.72	51.31	−8.1	−8.43	−8.00	−6.73	−5.83	−4.77	−2.70
Bc1o22e2	23.47	51.21	−8.60	−8.89	−8.31	−7.00	−6.09	−5.05	−2.11

[a] ΔH°_{f298} in kcal mol^{-1}; S°_{298} and $C_p(T)$ in cal mol^{-1} K^{-1}.
[b] Groups are intrinsic and do not include symmetry or optical isomer corrections.
[c] Benson[32] also used by Holmes and Lossing,[33] Turecek and Havelas[34] and Cohen[35].
[d] Chen and Bozzelli[36].
[e] Turecek and Havelas;[34] also used by Zhu *et al.*[16]

Table 15. Groups and their values, example use of group additivity for properties of Bc01o4e2[a]

No.	Group	ΔH°_{f298}	S°_{298}	$C_p(T)$						
				300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
1	2 C_D/C/H	17.18[d]	15.94[d]	8.32[d]	10.06[d]	11.62[d]	13.00[d]	15.3[d]	16.9[d]	19.24[d]
2	C/C/C$_D$/H/O	−6.00	−11.10	4.47	6.82	8.45	9.17	10.24	10.80	11.02
3	O/C$_2$	−23.20	8.68	3.40	3.70	3.70	3.80	4.40	4.60	4.80
4	C/C$_2$/H/O	−7.20	−11.00	4.80	6.64	8.10	8.73	9.81	10.40	11.51
5	C/C$_2$/H$_2$	−4.93	9.42	5.50	6.95	8.25	9.35	11.07	12.34	14.20
6	C/C/C$_D$/H$_2$	−4.76	9.80	5.12	6.86	8.32	9.49	11.22	12.48	14.36
	Sum (groups above[a])	−28.91	21.74	31.61	41.03	48.44	53.54	62.04	67.52	75.13
	Bc01o4e2 molecule[b]	0.21	76.25	24.55	33.15	40.66	46.89	56.18	62.70	72.40
	Bc01o4e2 ring group[c]	29.12	54.51	−7.06	−7.88	−7.75	−6.65	−5.86	−4.82	−2.73

[a] C_p or ΔH°_{f298} equals sum of the corresponding groups, S°_{298} equals sum of the corresponding groups – $R\ln(\sigma)$;–$R \ln$(symmetry); $R = 1.987$ cal mol^{-1} K^{-1}.
[b] C_p, S°_{298} and ΔH°_{f298} of the cyclic compounds from the B3LYP/6–31g(d,p) calculations on the bicyclic molecule.
[c] Bicyclic ring group calculated by difference.
[d] Numbers shown = 2 × group value.

CONCLUSION

Thermodynamic properties of oxabicycloheptenes were calculated using the density functional method in computational chemistry with several reaction schemes for cancellation of errors. Standard enthalpies of formation, $\Delta H^{\circ}_{f(298)}$s, were calculated using isodesmic reaction schemes based on the B3LYP/6–31G(d,p) calculation level with several reaction schemes for cancellation of errors. Entropies, S°_{298}, and heat capacities, $C_p(T)$s (10 K $\leq T \leq$ 5000 K), were obtained from B3LYP/6–31G(d,p)-optimized geometries and frequencies. Benson group additivity parameters for the different bicyclic ring structures were calculated for use in estimating larger (branched) molecules with the respective base structure.

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