Anharmonic Thermochemistry of Cyclopentadiene Derivatives

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ABSTRACT: This paper focuses on the thermochemistry of some derivatives of cyclopenta-1,3-diene, namely, 5-methylcyclopenta-1,3-diene, 5-ethylcyclopenta-1,3-diene, 5-formylcyclopenta-1,3-diene, 5-methylcyclopenta-1,3-diene-1-yl radical, 5-ethylcyclopenta-1,3-diene-1-yl radical, 5-carbonylcyclopenta-1,3-diene radical, 1-formylcyclopenta-2,4-diene-1-yl radical, 5-methylenecyclopenta-1,3-diene radical, 5-ethylidenecyclopenta-1,3-diene radical, and 3,6-dimethylenecyclohexa-1,4-diene. Several different chemistries of these compounds are of interest in combustion modeling. Here, we present gas-phase thermochemical properties for the above cited species, which are, except for 3,6-dimethylenecyclohexa-1,4-diene, previously unknown. These were obtained from corrected (using bond additivity corrections) high-level ab initio quantum chemistry calculations validated with well-known compounds including cyclopentane, cyclopentene, cyclopenta-1,3-diene, and cyclopentadienyl radical. Heat capacities and entropies have been corrected for anharmonic molecular motions, in particular for internal rotations. © 2003 Wiley Periodicals, Inc. Int J Chem Kinet 35: 453–463, 2003

INTRODUCTION

Cyclopentadienic compounds are important intermediates in the thermal decomposition and oxidation of monocyclic aromatic hydrocarbons. The oxidation of benzene and monosubstituted monoaromatics yields large amounts of cyclopenta-1,3-diene [1–3], whereas the oxidation of polysubstituted aromatics yields substituted cyclopentadienes. The subsequent oxidation of these compounds produces oxygenated derivatives of cyclopentadiene. However, there are relatively limited data in the literature concerning the kinetics and pathways of reactions involving these compounds. In some cases, thermochemical data are also lacking, and this limits further investigations concerning the combustion chemistry of monocyclic aromatic hydrocarbons. Karni et al. [4] performed ab initio calculations for several cyclopentadienic compounds and derived some thermodynamic data such as the enthalpy of formation. However, the Hartree–Fock method used by Karni et al. does not generally provide chemically accurate values for energetic quantities. Their calculations have been improved by Wang and Brezinsky [5],

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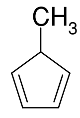
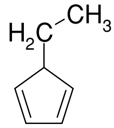
who used the G2 method and some methods derived from it. To avoid the computational expense of ab initio calculations, group additivity methods can be used to estimate the enthalpy of formation for species that have not been studied experimentally or theoretically [6]. However, as pointed out by Burcat and Gardiner [7], group additivity cannot be used for many cases, or can only be used with high uncertainty, because of the lack of group data, especially for radicals. Such an attempt concerning some cyclopentadienic species can be found in a study performed by Zhong and Bozzelli [8]. Despite the efforts cited above, there are species in this system for which neither theoretical nor experimental values are available in the literature, such as 5-ethylcyclopenta-1,3-diene, 5-formylcyclopenta-1,3-diene, and related radicals.

The aim of the present work is to use high-level (chemically accurate) quantum chemistry-based methods to compute the thermodynamic data (enthalpy of formation, standard entropy, and temperature-dependent heat capacity) for the following species:

5-methylcyclopenta-1,3-diene (a), 5-ethylcyclopenta-1,3-diene (b), 5-formylcyclopenta-1,3-diene (c), 5-methylcyclopenta-1,3-diene-1-yl radical (d), 5-ethylcyclopenta-1,3-diene-1-yl radical (e), 5-carbonylcyclopenta-1,3-diene radical (f), 1-formylcyclopenta-2,4-diene-1-yl radical (g), 5-methylenecyclopenta-1,3-diene radical (h), 5-ethylidenecyclopenta-1,3-diene radical (i), and 3,6-dimethylenecyclohexa-1,4-diene, or *p*-xylylene (j). Experimental thermodynamic properties of these species, except for species (j), have not been presented previously. Estimated thermodynamic properties have been presented previously for species (a) (see http://herzberg.ca.sandia.gov/~melius).



(a)



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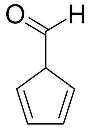

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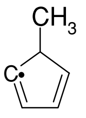
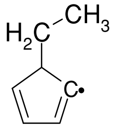
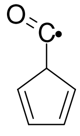


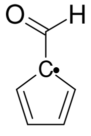
(d)



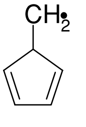
(e)



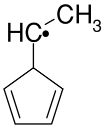
(f)



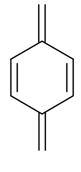
(g)



(h)



(i)



(j)

COMPUTATIONAL METHODS—ACCURACY OF THE STANDARD G2 METHOD AND ACCURACY OF THE CORRECTION METHODS APPLIED TO IT

Ab initio molecular orbital calculations have been performed for all the species given above, including the well-known cyclopentane, cyclopentene, and cyclopenta-1,3-diene that can be used to verify the validity of the calculations. The G2 methods used here have been shown to be reliable for a wide range of molecules, radicals, and ions, by Ochterski et al. [9], Petersson et al. [10], and many others. These methods are well described elsewhere [10]. The enthalpies of formation presented here were calculated based on the enthalpies of atomization computed from the ab initio calculations and the experimental heats of formation of gas-phase atoms at 298.15 K and 1 bar (52.10 kcal mol^{-1} for H, 171.21 kcal mol^{-1} for C, and 59.43 for O). The computed energies of the carbon atom and oxygen atom were corrected to account for spin–orbit coupling using the experimental spin–orbit interaction energies (0.0847 kcal mol^{-1} for C, and 0.223 kcal mol^{-1} for O [11]).

From the collection of Petersson et al. [10] of around 150 molecules with well-established experimental heats of formation, the results obtained using the G2 method are expected to be accurate to within ±1 to 2 kcal mol^{-1}, and for many species the standard G2 method itself is sufficiently accurate without application of any of the available bond additivity correction (BAC) methods. However, only a few cyclic compounds have been included in the test set of Petersson et al. [10] (see Table I). These species are moreover all hydrocarbons. Although this data set is quite limited, one can remark in Table I that the standard G2 method is expected to be accurate to within ±3 kcal mol^{-1} for the monocyclic hydrocarbons. Preliminarily, in fact, the accuracy seems to be better for the saturated monocyclic hydrocarbons than for the unsaturated ones and therefore the unsaturated monocyclic hydrocarbons are species for which the accuracy of the standard G2 method may not be sufficient. Since then, a new theoretical procedure, called G3, which modifies the G2 theory has been proposed [12]. Although this G3 procedure is more powerful than the standard G2 in general, it appears that the use of the G3 theory instead of the G2 theory does not result in much improvement for the monocyclic hydrocarbons cyclopentane, cyclobutane, cyclopentene, and cyclobutene. However, as indicated in Table I, the isodesmic BACs, applied to the standard, or raw, G2 calculations, established by Petersson et al. [10] allow about equally reliable estimations of the enthalpy of formation for the monocyclic

Table I Deviation Between Experiments and Uncorrected G2 Calculations, BAC G2 Calculations [10], and Uncorrected G3 Calculations [12] for Monocyclic Hydrocarbons

Molecule	Experimental Enthalpy of Formation at 298.15 K [10]	Deviation (Experiment − Theory) at 298.15 K at the Standard G2 Level [10]	Deviation (Experiment − Theory) at 298.15 K After BACs [10]	Deviation (Experiment − Theory) at 298.15 K at the G3 Level [12]
Cyclopropane	12.7 ± 0.1	−1.2	−0.3	−0.7
Cyclobutane	6.6 ± 0.3	−0.7	0.4	0.0
Cyclopropene	66.2 ± 0.6	−3.2	−1.5	−2.2
Cyclobutene	37.5 ± 0.4	−3.1	−1.2	−2.1
Methylene cyclopropane (C_4H_6)	47.9 ± 0.4	0.0	1.9	1.5
Cyclopentane	−18.3 ± 0.2	–	0.0	–

Units are kcal mol^{-1}.

species as the G3 theory. Wang and Brezinsky [5] have shown the reliability of the G2 method and its variations for the calculations of thermodynamic data for cyclopentadienic species. Unfortunately, the correction procedure of Petersson et al. [10] cannot be applied to the radical species, but only to closed-shell species. Therefore, the BAC-G2 correction method of Melius and Allendorf [13] was also used here. The BAC-G2 method also applies corrections to the standard G2 method, and its accuracy has been demonstrated for neutrals including closed as well as open-shell species (radicals). However, to assess further the reliability of the G2 method and also the reliability of the two above correction methods for the class of species under consideration here, some well-known molecules have been included in this study, namely cyclopentane, cyclopentene, and cyclopenta-1,3-diene.

RESULTS AND DISCUSSION

Table II gives the experimental and computed enthalpy of formation for the three test species. Without corrections, the computed enthalpies of formation are about 1.6, 2.5, and 3.5 kcal mol^{-1} higher than the experimental ones for cyclopentane, cyclopentene, and cyclopenta-1,3-diene, respectively. The preliminary statement above that the standard G2 method is not sufficiently accurate for unsaturated monocyclic hydrocarbons is confirmed in these three cases. By using the isodesmic BACs, the agreement between computations and experiments is very good, the absolute deviation being less than 0.5 kcal mol^{-1}. It appears that the correction procedure of Petersson et al. [10] can be applied with confidence to estimate the thermodynamic data of species not included in their test set. For the BAC-G2 method [13], the agreement between calculation and experiment is also good, the absolute deviation being less than 1 kcal mol^{-1}, and both methods are globally sufficiently accurate to predict reliable enthalpies of formation.

Consequently, the BAC method of Petersson et al. [10] has been used to estimate the enthalpies of formation of all closed-shell species, namely species (a), (b), (c), and (j), and the BAC-G2 method has been used to estimate the enthalpies of formation of all the

Table II Comparison Between Experiments and Standard or BAC Calculations at the G2 Level for Cyclopentane, Cyclopentene, and Cyclopenta-1,3-diene

Molecule	Experimental Enthalpy of Formation at 298.15 K	Enthalpy of Formation Calculated at 298.15 K with the Standard G2 Method	Enthalpy of Formation Calculated at 298.15 K at the G2 Level with Petersson's BACs [10]	Enthalpy of Formation Calculated at 298.15 K at the G2 Level with Melius' BACs
Cyclopentane	−18.48 [14] −18.3 ± 0.2 [10]	−16.73	−18.23	−18.59
Cyclopentene	8.2 [15] 8.2 [16]	10.71	8.44	8.6
Cyclopenta-1,3-diene	31.9 [16] 32.1 ± 0.4 [17]	35.41	32.37	33.06

Units are kcal mol^{-1}.

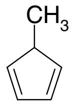
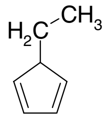
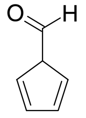
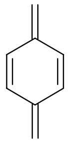
species, including the open-shell species. The results of these calculations are given in Table III for closed-shell species and in Table IV for radicals.

To the best of our knowledge, no experimental data can be found in the literature for species (a), (b), and (c). Concerning the *p*-xylylene, there is only one experimental determination of its heat of formation [16] and our calculations are consistent with the experimental result (see Table III).

In Table IV, the cyclopentadienyl radical has been introduced as a test case. In fact, the situation is quite complicated concerning the enthalpy of formation of this species as the reported experimental measurements range from 45 to 63 kcal mol^{-1}. DeFrees et al. [19] give a value of 63 ± 2 kcal mol^{-1} and the result presented here (65.7) is consistent with this experimental value. More on this subject has been recently discussed by Moskaleva and Lin [21] and Kiefer et al. [22]. However, it is worthwhile to note that the cyclopentadienyl radical exhibits some spin contamination (by states of higher multiplicity) at the standard G2 level with a spin-squared operator of about 1 instead of 0.75 (the value for a pure doublet). For species with mild spin contamination, i.e. with a spin-squared operator within about 0.05 of the value for the pure spin state, Mayer et al. [23] showed that the standard G2 method performs well, giving reliable predictions of thermochemistry. However, for more severely spin-contaminated species, the potential errors in G2 theory can climb to 5 kcal mol^{-1} or more, and the standard G2 enthalpy of formation for the radical (68.6 kcal mol^{-1}) is consistent with this statement. No explicit spin contamination-correction is introduced in the BAC-G2 method, but this method is shown to be more reliable than the BAC-hybrid methods [13] for which spin-contamination corrections are used for open-shell species. On the basis of reasonable agreement between experiments and BAC-G2 calculations for the cyclopentadienyl radical, these BAC-G2 calculations applied to spin-contaminated species can be expected to be reasonably accurate. This also holds for radicals with low levels of spin-contamination as stated above following Mayer et al. [23].

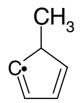
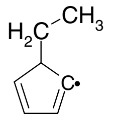
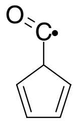
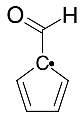
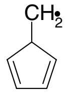
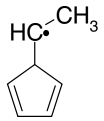
The calculations at the standard G2 level for the species (e) and (i) are too computationally expensive for us to perform at present. Thus, the enthalpies of formation for these two species have been calculated at the standard G2MP2 level. This method has been shown by Petersson et al. [10] to be less accurate than the standard G2 method with a mean abolute deviation of 1.76 kcal mol^{-1} for the G2MP2 method for neutrals, including both molecules and radicals, compared to 1.43 kcal mol^{-1} for the standard G2 method. No BAC procedure is available to us at this time for the G2MP2 method.

Table III Comparison Between Experiments and Raw or BACs or BAC-G2 Calculations at the G2 Level for Compounds (a), (b), (c), and (j)

Molecule	Experimental Enthalpy of Formation at 298.15 K	Enthalpy of Formation Calculated at 298.15 K at the G2 Level	Enthalpy of Formation Calculated at 298.15 K at the G2 Level with Petersson's BACs	Enthalpy of Formation Calculated at 298.15 K at the G2 Level with Melius' BACs (BAC-G2)
	–	29.43	25.89	26.70
	–	24.42	20.58	21.32
	–	9.23	6.25	7.33
	50 ± 4 [18]	58.02	52.54	54.06

Units are kcal mol^{-1}.

Table IV Comparison Between Experiments, Raw G2, and BAC-G2 Calculations for Cyclopentadienyl Radical and Compounds (d), (e), (f), (g), (h), and (i)

Molecule	Experimental Enthalpy of Formation at 298.15 K	Enthalpy of Formation Calculated at 298.15 K with the Standard G2 Method	Enthalpy of Formation Calculated at 298.15 K at the G2 Level with Melius' BACs
	63 ± 2 [19] 62.5 ± 1 [20]	68.60[a]	65.70
	–	96.39[a]	93.30
	–	92.80 [b,c]	[d]
	–	49.33[e]	46.58
	–	68.32[e]	65.85
	–	80.79[e]	77.32
	–	75.50[b,f]	[d]

Units are kcal mol^{-1}.

[a] Calculations show some moderate or high spin-contamination at the standard G2 level.

[b] Calculations performed at the standard G2-MP2 level.

[c] Calculations show some moderate or high spin-contamination at the standard G2-MP2 level.

[d] No correction procedure available for standard G2-MP2 level.

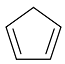
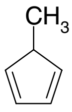
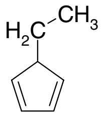
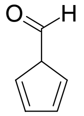
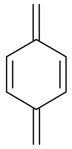
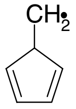
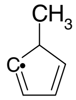
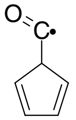
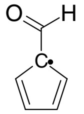
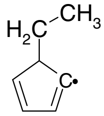
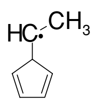
[e] Calculations show low spin-contamination at the standard G2 level.

[f] Calculations show low spin-contamination at the standard G2-MP2 level.

BOND LENGTHS AND ANGLES AND VIBRATIONAL FREQUENCIES

Scaled B3LYP/6-31G(d) vibrational frequencies, from which heat capacities can be derived, are given in Table V. The agreement between experimental data and ab initio computations of vibrational frequencies and bond lengths at this level of theory has been shown to be good for a wide range of molecules [24,25]. Scott and Radom [25] report that one of the most successful procedures for obtaining fundamental vibrational frequencies is to use scaled frequencies computed at the B3LYP/6-31G(d) level of theory as done here. The bond lengths and angles in the molecules studied are not reported here, but can be obtained from the authors upon request. To briefly demonstrate the reliability of the bond lengths and angles computed by using the B3LYP/6-31G(d) method, Fig. 1 gives the experimental bond lengths and angles as well as the computed ones here for cyclopenta-1,3-diene. Good agreement

Table V Computed and Experimental (if any) Vibration Frequencies and Computed Moments of Inertia for the Species Under Consideration in This Study

Species	Spin State	Scaled Vibrational Frequencies (cm^{-1})[a,b]	Moments of Inertia (amu bohr^2)
Cyclopenta-1,3-diene 	Singlet	336[350] 501[516] 661[664] 683[700] 781[802] 782[805] 894[891] 895[915] 913[925] 919[941] 941[959] 983[994] 1081[1090] 1089[1100] 1096[1106] 1233[1239] 1280[1292] 1364[1365] 1391[1378] 1514[1500] 1597[1580] 2909[2886] 2932[2900] 3085[3043] 3095[3075] 3113[3091] 3119[3105]	213 219 422
	Singlet	159 **249** 278 520 539 689 693 754 778 840 914 914 920 964 990 1043 1060 1081 1107 1228 1248 1281 1361 1380 1469 1469 1516 1597 2877 2931 2993 3007 3081 3090 3106 3113	257 509 690
	Singlet	**98** 141 201 **251** 363 505 546 685 693 732 781 808 847 913 917 922 970 982 1013 1061 1068 1081 1112 1205 1218 1274 1293 1326 1368 1384 1458 1469 1476 1515 1598 2868 2922 2927 2959 2990 2997 3082 3092 3108 3116	291 963 1167
	Singlet	**77** 105 326 426 498 550 705 721 787 804 907 920 922 931 985 996 1005 1082 1092 1158 1214 1273 1361 1366 1490 1584 1747 2824 2979 3092 3103 3121 3126	267 894 1053
	Singlet	104 262 311 362 380 447 464 603 629 679 716 754 777 807 812 855 864 924 943 945 961 966 1123 1171 1279 1324 1333 1387 1416 1446 1563 1578 1618 1651 3045 3046 3052 3053 3070 3073 3125 3125	344 1115 1459
	Doublet	**111** 150 277 472 528 546 696 698 750 776 835 912 917 954 974 995 1058 1078 1105 1172 1244 1268 1358 1420 1507 1593 2894 3047 3084 3095 3116 3120 3147	253 483 658
	Doublet	151 **251** 268 464 532 671 730 748 800 838 896 904 946 995 1049 1054 1093 1181 1215 1252 1302 1378 1468 1470 1503 1590 2902 2938 3003 3014 3078 3102 3114	237 515 675
	Doublet	**21** 115 336 396 458 549 695 699 783 800 860 907 922 925 966 987 1082 1091 1133 1197 1272 1363 1499 1590 1827 2926 3096 3107 3127 3131	254 901 1075
	Doublet	**136** 187 269 374 489 512 579 699 711 787 823 867 871 948 983 985 1057 1154 1221 1264 1348 1367 1434 1529 1702 2795 3106 3117 3125 3138	228 909 1138
	Doublet	**100** 141 186 **247** 349 483 515 668 727 751 787 805 848 902 927 945 955 1015 1063 1064 1099 1172 1203 1219 1285 1304 1323 1383 1458 1466 1475 1502 1590 2894 2926 2927 2963 2992 2999 3079 3102 3114	276 959 1148
	Doublet	**52 103** 123 252 346 472 504 547 696 696 776 794 856 909 917 924 962 976 988 1054 1078 1084 1123 1174 1203 1268 1341 1359 1382 1444 1457 1507 1593 2841 2873 2930 2981 3059 3083 3094 3113 3118	269 996 1177

[a] Experimental data are in brackets.

[b] Bold frequencies indicate internal rotations for the species considered.

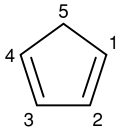


Figure 1 Comparison between the experimental (exp) and computed (comp) C–C bond lengths and <CCC bond angles in cyclopenta-1,3-diene. C1–C5 and C4–C5: 1.509 Å (exp), 1.507 Å (comp); C3–C4 and C1–C2: 1.342 Å (exp), 1.349 Å (comp); C2–C3: 1.469 Å (exp), 1.470 Å (comp); <C2C1C5 and <C3C4C5: 109.3° (exp), 109.1° (comp); <C2C3C4 and <C1C2C3: 109.4° (exp), 109.3° (comp); <C1C5C4: 102.8° (exp), 103.2° (comp).

between experiment and theory is clearly shown here and can be expected as well for all the species studied here. In Table V, the scaled (by 0.9613 as recommended by Scott and Radom [25]) computed frequencies are given for the species studied here. They are compared to experimental data for cyclopenta-1,3-diene, the only species in the table for which experimental data were available. The average absolute deviation is only 16 cm^{-1}. Therefore, it can be concluded that the methods used here allow the reliable computation of the vibrational frequencies (and therefore also of the zero-point energy, heat capacity, and standard entropy calculated from those frequencies) with useful accuracy.

THERMODYNAMIC DATA

Harmonic Treatment

The thermochemical data described above are summarized in Table VI. The thermochemical calculations (to get the heat capacity, etc.) were carried out using the GAUSSIAN 94 [26] and GAUSSIAN 98 [27] computational chemistry programs that were also used for the ab initio quantum chemical calculations. In Table VI, the entropy and heat capacity are calculated following the harmonic oscillator approximation. This approximation is usually the one used in the combustion chemistry field but, at high temperature, errors can result if the harmonic oscillator approximation is used for low-frequency modes that represent hindered internal rotations or free internal rotations [28,29].

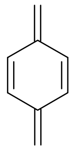
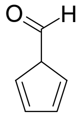
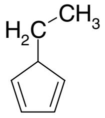
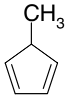
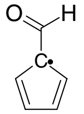
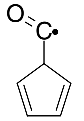
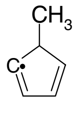
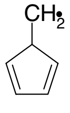
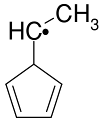
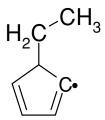
Anharmonic Treatment

Internal Rotations. As the partition function for a harmonic oscillator and for a free or hindered rotor are quite different, some corrections to the heat capacity and entropy are needed. For this study, the normal vibrational modes corresponding to internal rotations are identified at the B3LYP/6-31G(d) level of theory by using the procedure of Ayala and Schlegel [28] as implemented in Gaussian 98. The heat capacity and entropy are then corrected using the tables of Pitzer and Gwinn as given in Ref. [30]. Table V gives for each species the frequencies of the vibrational modes that correspond to hindered internal rotations. These modes have been treated anharmonically and the resulting anharmonic thermochemistry is given in Table VI. For C_v, the maximum correction is $R/2$, i.e. 0.993 cal mol^{-1} K^{-1} per vibrational mode treated as an internal rotation. However, this maximum correction is only observed at high temperature (above 2000 K) for most of the species studied here and here the anharmonic heat capacity remains within about 3% of the harmonic one in the 298–1500 K temperature range considered here (see Table VI). Even for the most strongly anharmonic species, namely species (i) for which the two internal rotations are still strongly anharmonic at ambient temperature, the maximum deviation is less than 4% from harmonicity in the 298–1500 K temperature range (see Table VI). Moreover, the maximal deviation in percent (or relative deviation) from harmonicity for this species is observed in the 300–500 K temperature range (i.e. for conditions generally not of interest for combustion) and, if the absolute deviation from harmonicity tends to about R/2 per rotor at 1500 K (maximum absolute deviation from harmonicity is −1.93 cal K^{-1} mol^{-1} for species (i) at 1500 K), the corresponding deviation from harmonicity is only 2.5% of the total heat capacity (see Table VI) for species (i). However, for most of the species considered here the relative deviation from harmonicity is in fact lower at combustion temperature than at ambient temperature.

For entropy, the relative deviation from harmonicity for all the species considered here is less than 1% at 298 K (see Table VI). At higher temperature, the relative deviation from harmonicity for entropy is given in Table VII. The maximum absolute deviation from harmonicity is −2.33 cal K^{-1} mol^{-1} for species (i) at 1500 K. The maximum relative deviation from harmonicity is 1.3% (species (i)) in the 298–1500 K temperature temperature range.

Pseudorotation. Some other types of anharmonic motion exist that are characteristics of ring molecules. Among these types, pseudorotation, which is a concerted motion of several atoms along a periodic coordinate [29], is observed in n-membered rings, where n is the number of atoms in the ring and is at least five. Unsaturated rings behave much like a saturated ring of size (n–m) where m is the number of double bonds [31]. Cyclopentadiene derivatives as doubly bonded molecules are therefore not pseudorotating molecules since a three-membered ring has no pseudorotation

Table VI Harmonic (Values in Italic) and Anharmonic (Values in Bold) Thermochemical Data

		C_V						
Species	S° (298 K)	300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
	*78.51*[a]	*28.31*	*37.65*	*45.33*	*51.51*	*60.65*	*67.07*	*76.61*
	*79.36* **79.53** (+0.2)[b]	*22.97* **23.33** (+1.6)	*30.54* **30.82** (+0.9)	*36.86* **36.98** (+0.3)	*41.92* **41.85** (−0.2)	*49.29* **48.88** (−0.8)	*54.38* **53.84** (−1)	*61.80* **61.03** (−1.2)
	*81.97* **82.54** (+0.7)	*27.13* **27.82** (+2.6)	*36.71* **37.30** (+1.6)	*45.01* **45.39** (+0.8)	*51.84* **51.88** (+0.1)	*62.15* **61.57** (−0.9)	*69.51* **68.56** (−1.4)	*80.55* **79.14** (−1.8)
	*74.44* **74.64** (+0.3)	*22.04* **22.37** (+1.5)	*30.02* **30.38** (+1.2)	*36.85* **37.10** (+0.7)	*42.41* **42.51** (+0.2)	*50.74* **50.56** (−0.3)	*56.66* **56.24** (−0.7)	*65.53* **64.88** (−1)
	*79.38* **79.41** (+0.1)	*23.31* **23.39** (+0.3)	*30.13* **30.24** (+0.3)	*35.71* **35.84** (+0.4)	*40.14* **40.33** (+0.5)	*46.54* **46.82** (+0.6)	*50.92* **51.27** (+0.7)	*57.27* **57.51** (+0.4)
	*83.25* **83.43** (+0.2)	*22.84* **22.08** (−3.3)	*29.75* **28.91** (−2.8)	*35.41* **34.53** (−2.5)	*39.87* **38.96** (−2.3)	*46.32* **45.37** (−2.1)	*50.73* **49.77** (−1.9)	*57.15* **56.17** (−1.7)
	*75.82* **75.94** (+0.2)	*21.53* **21.82** (+1.4)	*28.83* **29.18** (+1.2)	*35.05* **35.32** (+0.8)	*40.10* **40.20** (+0.3)	*47.65* **47.47** (−0.4)	*52.97* **52.68** (−0.6)	*60.91* **60.26** (−1.1)
	*77.86* **78.21** (+0.5)	*22.97* **22.44** (−2.3)	*30.40* **29.74** (−2.2)	*36.51* **35.75** (−2.1)	*41.36* **40.52** (−2)	*48.50* **47.60** (−1.9)	*53.53* **52.60** (−1.7)	*61.12* **60.16** (−1.6)
	*86.56* **87.07** (+0.6)	*27.68* **26.73** (−3.4)	*36.63* **35.22** (−3.8)	*44.26* **42.66** (−3.6)	*50.45* **48.77** (−3.3)	*59.72* **57.88** (−3.1)	*66.29* **64.41** (−2.8)	*76.15* **74.21** (−2.5)
	*83.40* **83.91** (+0.6)	*26.63* **27.27** (+2.4)	*35.53* **36.16** (+1.8)	*43.24* **43.69** (+1)	*49.56* **49.73** (+0.3)	*59.09* **58.61** (−0.8)	*65.85* **65.02** (−1.3)	*75.94* **74.53** (−1.9)

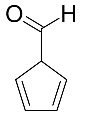
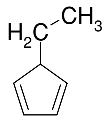
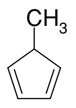
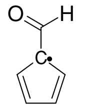
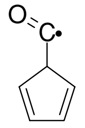
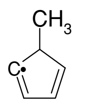
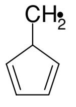
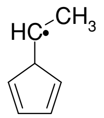
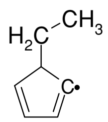
Corrections result from the consideration of internal rotations. Units are cal K^{-1} mol^{-1}. Enthalpies of formation at 298 K are given in Tables III and IV.

[a] No correction due to internal rotations.

[b] Numbers in parentheses are the relative deviation to harmonicity (given in %).

mode. This holds for closed-shell species (species (a), (b), (c), and also (j)). However, open-shell molecules, such as the cyclopentadienyl radical, exhibit pseudorotation (Jahn–Teller distortion). Kiefer et al. [22] recently showed that the replacement of the lowest harmonic frequency with a one-dimensional free rotor for cyclopentadienyl radical leads to reliable estimates of the entropy compared to their comprehensive

Table VII Harmonic (Values in Italic) and Anharmonic (Values in Bold) Thermochemical Data for Entropy

	$S°$					
Species	400 K	500 K	600 K	800 K	1000 K	1500 K
	*87.75* **87.98** (+0.3)[a]	*95.72* **96.14** (+0.4)	*103.27* **103.66** (+0.4)	*116.98* **117.31** (+0.3)	*129.00* **129.14** (+0.1)	*153.45* **153.33** (−0.1)
	*91.85* **92.52** (+0.7)	*101.41* **102.27** (+0.8)	*110.60* **111.57** (+0.9)	*127.59* **128.26** (+0.5)	*142.74* **143.30** (+0.4)	*174.09* **174.14** (+0.0)
	*82.62* **82.94** (+0.4)	*90.52* **90.97** (+0.5)	*98.11* **98.61** (+0.5)	*112.10* **112.55** (+0.4)	*124.54* **124.88** (+0.3)	*150.21* **150.30** (+0.1)
	*87.78* **87.89** (+0.1)	*95.57* **95.64** (+0.1)	*102.85* **102.96** (+0.1)	*115.91* **115.91** (0)	*127.24* **127.49** (+0.2)	*150.06* **150.45** (+0.3)
	*91.52* **91.44** (−0.1)	*99.24* **98.96** (−0.3)	*106.47* **106.02** (−0.4)	*119.46* **118.75** (−0.6)	*130.74* **129.82** (−0.7)	*153.50* **152.18** (−0.9)
	*83.75* **84.01** (+0.3)	*91.31* **91.68** (+0.4)	*98.53* **99.03** (+0.5)	*111.74* **112.19** (+0.4)	*123.42* **123.68** (+0.2)	*147.40* **147.49** (+0.1)
	*86.24* **86.34** (+0.1)	*94.15* **94.09** (−0.1)	*101.61* **101.47** (−0.1)	*115.13* **114.51** (−0.5)	*126.96* **126.27** (−0.5)	*151.09* **150.02** (−0.7)
	*96.52* **96.58** (+0.1)	*105.99* **105.71** (−0.3)	*114.99* **114.41** (−0.5)	*131.43* **130.19** (−0.9)	*145.94* **144.37** (−1.1)	*175.73* **173.40** (−1.3)
	*93.05* **93.69** (+0.7)	*102.28* **103.10** (+0.8)	*111.10* **112.02** (+0.8)	*127.32* **128.03** (+0.6)	*141.72* **142.33** (+0.4)	*171.38* **171.56** (+0.1)

Corrections result from the consideration of internal rotations. Units are cal K^{-1} mol^{-1}. Enthalpies of formation at 298 K are given in Tables III and IV.

[a] Numbers in parentheses are the relative deviation to harmonicity (given in %).

Jahn–Teller effect model. This was also done here, as for about all the open-shell species the lowest vibration frequency has been identified as an internal rotation and therefore treated as anharmonic following a treatment which is equivalent with the assimilation of the internal rotation to a one-dimensional free rotor at high temperature. There is no way to see if this preliminary treatment is here sufficient because of the lack of experimental data. It is therefore possible that the entropy can be overestimated by about 1 cal K^{-1} mol^{-1} for some of the species presented here.

Ring Puckering. Another strongly anharmonic mode is ring puckering. However, as none of the B3LYP/6-31G(d) optimized geometry exhibits a puckered ring, no correction for this anharmonic mode is needed.

CONCLUSIONS

Computed thermodynamic data for cyclopentadiene-derived species are reported in this study. These data are needed to understand more deeply the role played by cyclopenta-1,3-diene and its derivatives during the combustion chemistry of some aromatic compounds. The standard G2 method has been used to get the thermochemical properties, but for cyclic unsaturated hydrocarbons this method needs to be corrected to provide chemically accurate predictions. This has been done using two correction procedures. The BAC-G2 correction method of Melius and Allendorf and the BAC correction method of Petersson et al. are shown to be consistent for molecules. For radicals, only the BAC-G2 correction method has been applied, because of the lack of applicability of the BAC correction method of Petersson et al. to open-shell species. It is not stated here that the BAC correction method of Petersson et al. is not valuable for open-shell species. The BAC-G2 method is expected to be reliable for the cyclic unsaturated radicals studied here based on the agreement between calculations and experiments for the cyclopentadienyl radical.

Heat capacities and entropies have been calculated and corrected for anharmonic molecular motions, in particular internal rotations. If one considers that the heat capacities and entropies are computed at ±2 cal K^{-1} mol^{-1}, then the corrections due to the neglect of internal rotations are not significant here (they are in the computational error). However, this statement is true here only because the number of rotors does not exceed two. Other strongly anharmonic molecular motions have also been examined, namely pseudorotation and ring puckering. Concerning pseudorotation, theoretical progress is needed to allow a full treatment to correct the open-shell species' thermochemistry for the effect of Jahn–Teller distortion. As such theoretical progress needs validation, experimental data are also needed.

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