Structural and Thermodynamic Properties of Diyttrium Carbides Y_2C_n ($n = 2-8$): A Theoretical Study

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Theoretical studies of diyttrium carbides Y_2C_n ($n = 1-8$) that included both relativistic and electron correlation effects are presented. Consideration of several alternative structures leads to cyclic structures as the ground-state structures. Using the theoretically computed partition functions, thermodynamic data are computed and the experimental Gibbs energy functions are corrected. The computed atomization energies of these species are close to the corrected experimental data. The Y−C bond is strongly ionic due to electron transfer from the yttrium atom to the carbon atom.

1. Introduction

Ever since the first observation by Chupka et al.,[1] gaseous transition-metal carbides have become a topic of several thermodynamic studies during the past three decades. Gaseous carbides are produced from mixtures of a metal powder and graphite in high-temperature ovens[2] or more recently by laser vaporization[3,4] techniques. Despite considerable interest in these systems, fueled in part by metallofullerenes,[5,6] there is little experimental information on the bonding of a metal atom with carbon clusters, even in simple model systems.[7] There is considerable controversy in the literature with regard to the structures of transition-metal carbides and their daughter cations, primarily due to scarcity of spectroscopic data on these species. Molecular structures had to be assumed for these species in the thermodynamical derivation of their properties on the basis of agreement between the second- and the third-law evaluations of experimental data.[8,9] Recent experimental studies[10,11] have employed injected ion drift tube techniques which have yielded the mobilities of gas-phase ions. It was deduced from the measured ion mobility data that there should be isomers for such transition-metal carbides. Some structural information is also available from the reactivity studies of metal carbide cations generated by a direct laser vaporization (DLV) technique.[12] While linear geometries seem to fit reasonably well with the thermodynamic data in the case of monometal carbides, the authors of other experiments suggest that even for a small number of carbon atoms ringlike structures are preferable.[10] In most cases theoretical studies on monometal carbides yield nonlinear structures as the ground states of these species.[13−15]

Dimetal carbides are observed in the same experiments that produce monometal carbides.[2,8,12] However, even less information is available about the molecular structures of these species. No reasonable second law values could be obtained for any M_2C_n species.[16] A recent theoretical study on $YIrC_2$ suggests a nonlinear ground-state structure.[17]

As evidenced from the above review, there is considerable uncertainty on the ground-state structures of M_2C_n even for small values of n. A primary objective of this work is to determine the equilibrium molecular structures of Y_2C_n from which the partition functions and thermodynamic properties are computed. Using the computed equilibrium structures, the partition functions, and the available experimental data,[18] the experimental atomization energies and the estimated Gibbs free energy functions are corrected. The nature of the metal−carbide bonds is also discussed.

2. Theoretical Methods and Computational Details

The calculations presented here were performed using density functional theory (DFT)[19] and Møller−Plesset second-order perturbation theory (MP2).[20] The DFT approach has utilized the Becke[21] (exchange) and the Lee−Yang−Parr[22] (correlation) functional. The geometry searches were made at the DFT and MP2 levels of theory by applying a quasi-Newton−Raphson procedure.[23,24] The calculations were performed using the spin-unrestricted Hartree−Fock (UHF) method, and the projected MP2 (PMP2) results free from spin contamination from other states are reported for the electronic states arising from open-shell electronic configurations.

All of the computations described here included relativistic effects[25] with the exception of spin−orbit coupling. The general techniques of relativistic computations and their applications have been reviewed elsewhere.[25] For the specific carbide clusters considered here, the calculations were made using the relativistic effective core potentials[26] (RECPs) that treated all but the $4s^24p^64d^15s^2$ shells in the core for yttrium and all but the $2s^22p^2$ shells in the core for the carbon atoms. We start with the [5s5p4d] valence Gaussian basis set for Y[26] and the [4s4p] valence Gaussian basis set for C.[26] The two largest exponent p and d functions of Y were contracted with the coefficients given in ref 26 for Y so that the basis set for Y becomes [5s5p4d/5s4p3d]. The two largest exponent s functions of C and the three tightest p functions of C were contracted with coefficients in ref 26 so that the C basis set is described as [4s4p/3s2p]. The carbon basis set was supplemented with a set of six-component 3d Gaussian functions adopted from Dunning and Hay.[27] For the yttrium atom we also tested the effect of 4f-type functions on Y_2C_2 with a 10-component 4f Gaussian function with exponent of 0.206. We found that 4f functions make a negligible difference in the computed proper-

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ties with the largest impact being on the dissociation energy. This is consistent with a previous study[28] which found that the 4f-type functions make only small contributions to energy separations. The dissociation energy of Y_2C_2 becomes 8.8 kJ/mol higher due to the 10-component 4f functions. The choice of atomic basis sets made here is based on previous computations for the monoyttrium carbides.[14] The basis set without 10-component 4f-type functions leads to 214 atomic orbitals for the largest molecule studied, namely, Y_2C_8. The choice of alternative electronic states for the ground states of Y_2C_n was governed by our previous study on YC_n.[14] The ground electronic states of monoyttrium carbides were found to be doublets.[14] The interaction with an additional yttrium atom in its ^2D electronic ground state would lead to both singlet and triplet electronic states for Y_2C_n, and thus both singlet and triplet electronic states of Y_2C_n are considered.

The calculations of thermodynamic functions were performed at the DFT level of theory by applying the ideal gas, rigid rotor, and harmonic oscillator approximations.[29] All available excited electronic states were included in the computations of the partition functions, but the contributions from excited electronic states to the partition functions are considerably smaller than those of excited vibrational and rotational states, as the of the energies of excited electronic states are higher. The computations were made using the Gaussian 94[30] code.

3. Molecular Structures of Diyttrium Carbides

Before we consider the equilibrium geometries of Y_2C_n clusters, let us compare our computed results for the experimentally known properties of the naked carbon clusters. Carbon clusters with fewer than 10 atoms are linear, although ring isomers are not ruled out,[31] especially for larger clusters. However, even for smaller number of carbon atoms, the reaction of these clusters with metals in most cases leads to nonlinear structures.[13−15] This indicates that the energetic gain due to multiple metal−carbon bonds with two carbon atoms circumvents the strain energy caused by bending the carbon chains. The approximate energetics of Y_2C_n isomers can be deduced from the bond energy values, which decrease in the order C═C (590 kJ/mol),[32] C═Y (414 kJ/mol),[33] C−Y (317 kJ/mol), and Y−Y (283 kJ/mol).[28] Since the number of possible isomers increases rapidly with the number of carbon atoms, all possible isomers were studied for the smaller carbides with the aim of deducing a pattern that would aid in the prediction of the most important isomers of larger clusters.

DFT optimization was performed for all isomers considered here. MP2 optimization was performed for the most probable candidates for the ground state, and the results were found to be close to the DFT optimized structures.

Y_2C. Three isomers have been found for this compound (Figure 1). The nonlinear C_{2v} structure in the singlet electronic state is the ground state. The triplet state is 0.47 eV above the ground state. The linear unsymmetrical isomer is also stable, but it is significantly (3.83 eV) higher in energy. Although experimental data are not available for this molecule, the La_2C analogue has been discovered and characterized thermodynamically.[34]

Y_2C_2. Figure 2 shows two structures considered as candidates for the ground state of Y_2C_2, namely, a linear isomer and a cyclic structure. The linear isomer in the singlet electronic state is only 0.04 eV lower than the cyclic structure in the triplet electronic state.

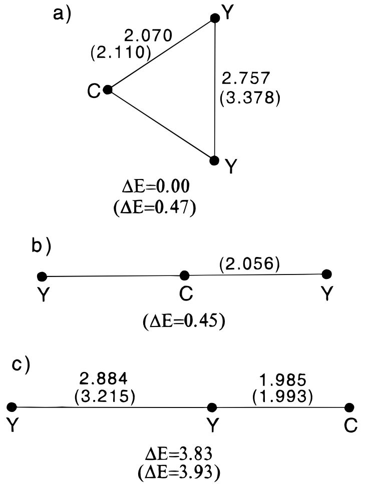

Figure 1. Equilibrium structures and energy separations (Δ*E*) from the DFT calculations for the singlet and triplet (values in parentheses) electronic states of Y_2C. Distances are in angstroms and energies in electronvolts. The values for nonequivalent bonds are given.

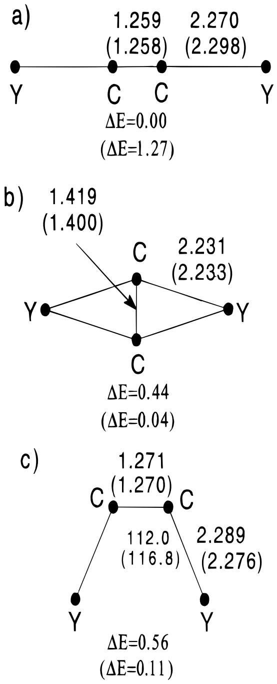

Figure 2. Equilibrium structures and energy separations (Δ*E*) from the DFT calculations for Y_2C_2. Values in parentheses correspond to the triplet electronic states, otherwise singlet electronic states. Distances are in angstroms and energies in electronvolts. Only nonequivalent results are presented.

The C-structure (triplet electronic state) (Figure 2c) is also very close to the ground state. The geometry optimization of a T-structure with the C═C fragment approaching perpendicular to the Y−Y dimer results in a cyclic isomer. On the other hand, a T-isomer with Y−Y approaching the C═C bond is 3.6 eV above the ground state. All other three-dimensional structures were found to be unstable, and geometry optimization leads to planar isomers.

Y_2C_3. Figure 3 shows four stable isomers that have been located for the Y_2C_3 cluster. The lowest isomer, namely, a cyclic isomer (singlet), is 0.45 eV lower than the singlet C-structure (Figure 3). The Y_2C_3 cyclic structure can be envisaged to be formed from Y_2C_2 by incorporating a carbon atom into the ring, but the structure with a carbon attached outside of the ring is also feasible and stable (Figure 3c). The linear singlet is stable but higher in energy. The structures that

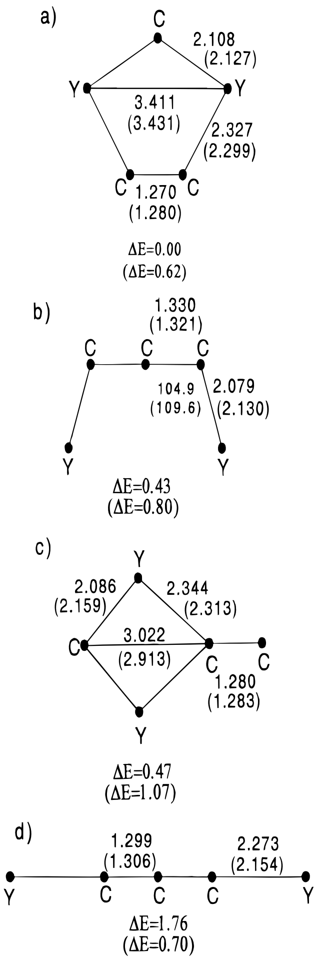

Figure 3. Equilibrium structures and energy separations (ΔE) from DFT calculations for the singlet and triplet (results in parentheses) electronic states of Y_2C_3. Distances are in angstroms and energies in electronvolts.

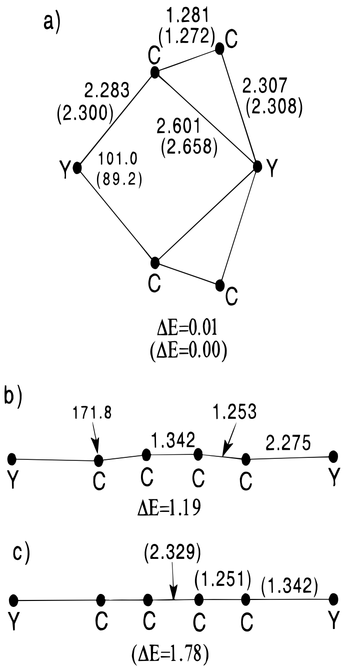

Figure 4. Equilibrium structures and energy separations (ΔE) from DFT calculations for the singlet and triplet (results in parentheses) electronic states of Y_2C_4. Distances are in angstroms and energies in electronvolts.

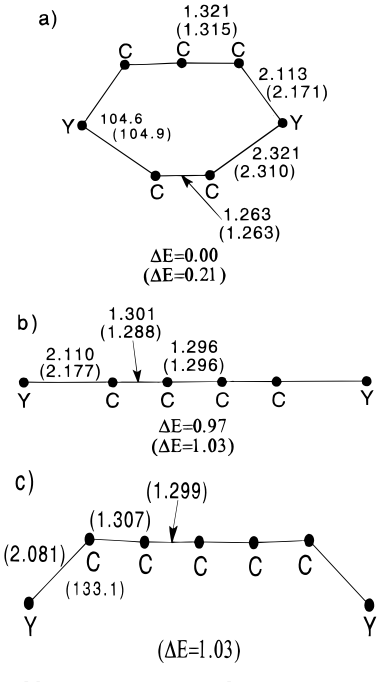

Figure 5. Equilibrium structures and energy separations (ΔE) for singlet and triplet (values in parentheses) electronic states of Y_2C_5. Calculations were performed at the DFT level. Distances are in angstroms and energies in electronvolts.

contain a direct Y−Y bond as well as other nonplanar structures were found to be unstable.

Y_2C_4. The cyclic singlet and triplet electronic states of Y_2C_4 are very close in energy (DFT, 0.01 eV; MP2, 0.17 eV), and both are candidates for the ground state. The next stable isomer with a singlet electronic state is the C-structure, which is higher in energy by 1.19 eV (Figure 4). The linear triplet state is 1.75 eV higher. No stable nonplanar isomers have been found.

Y_2C_5. On the basis of our computed results for the smaller carbides, the three isomers shown in Figure 5 were considered as candidates for Y_2C_5. The computed ground state is a singlet electronic state for the cyclic isomer. The linear and C-structures are about an electronvolt higher. A nonplanar structure derived from the cyclic isomer bent along the Y−Y axis goes to the energetically lower planar isomer during the geometry optimization process.

Y_2C_6, Y_2C_7, and Y_2C_8. Three cyclic structures, shown in Figure 6, were considered for Y_2C_n ($n = 6-8$) clusters. These structures are considered as the most probable isomers on the basis of the optimized structures of smaller clusters. In all three cases (Figure 6) triplet and singlet electronic states are separated by few tenths of an electronvolt.

4. Nature of Bonding and Its Influence on the Molecular Topology

Two major groups of topological structures have been determined for the diyttrium carbides, namely, the closed (cyclic) and open (linear or C) structures. As expected, none of the ground-state structures possess a Y−Y bond. In both cases carbon chains maintain geometries close to linear. In the cyclic isomers, yttrium atoms span two nearly linear chains. The open C-structure also has a linear carbon skeleton with bent terminal branches containing Y atoms. For the open structures, the stable linear isomer (singlet or triplet) is accompanied by the C-isomer in triplet or singlet states, respectively. This singlet−triplet rule originates from the degeneracy of the HOMOs for the linear chains. If both degenerate HOMOs are occupied in the singlet

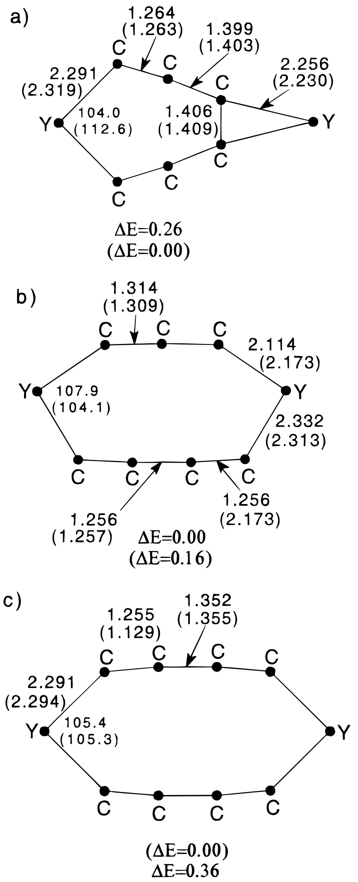

Figure 6. Equilibrium structures and energy separations (Δ*E*) from DFT calculations for Y_2C_6, Y_2C_7, and Y_2C_8. Values in parentheses correspond to the triplet electronic state, otherwise singlet electronic states. Energies are in electronvolts and distances in angstroms.

electronic state, the state remains linear. However, excitation to the triplet breaks the symmetry, and the molecule distorts to a symmetrically lower C-structure. In cases where only one degenerate HOMO is filled with a pair of electrons as in the singlet electronic state, the molecule distorts to lower symmetry, analogous to Jahn–Teller distortion. In the corresponding triplet state, as both degenerate HOMOs carry an electron, symmetry breaking does not occur, and the molecule remains linear. The singlet–triplet geometry swap is not a simple function of the odd–even number of carbon atoms in the molecule because the position of HOMOs depends on the number of inner molecular orbitals.

The Y–C bonds have considerable ionic character arising from transfer of an electron from the yttrium atom to the carbon chain. The stability of the Y center depends on the propensity of the carbon fragment to accept electronic density. An electron is donated by each of the yttrium atoms to the ring in the case of closed structures. In open structures, Y forms only one bond, and the charge donation is between 0.5 and 0.6 electron. The immediate neighbors of the yttrium atoms are influenced to a considerable extent by electron transfer. Both branches of carbon chains in the cyclic structures receive comparable electronic densities, although the distribution within the branches is influenced by the topology of the molecule (Figure 7). It should be noted that the Mulliken population can be altered by the 10-component 4f-type functions. In the case of Y_2C_2, we found that the inclusion of 4f-type functions decreases the atomic charge on Y from 0.7 to 0.6, suggesting enhanced electron transfer to the carbon chain. However, such subtle changes do not influence the overall trend and the extent of charge transfer.

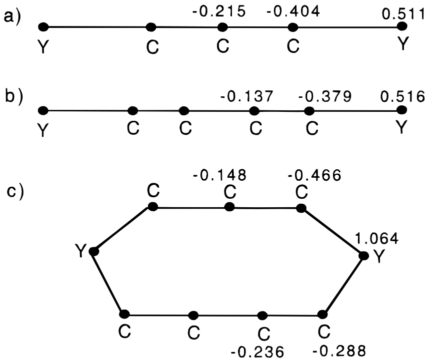

Figure 7. Atomic charges of nonequivalent atoms from the Mulliken population analysis for Y_2C_3 (a) and Y_2C_4 (b) open and Y2C7 (c) closed structures of diyttrium carbides.

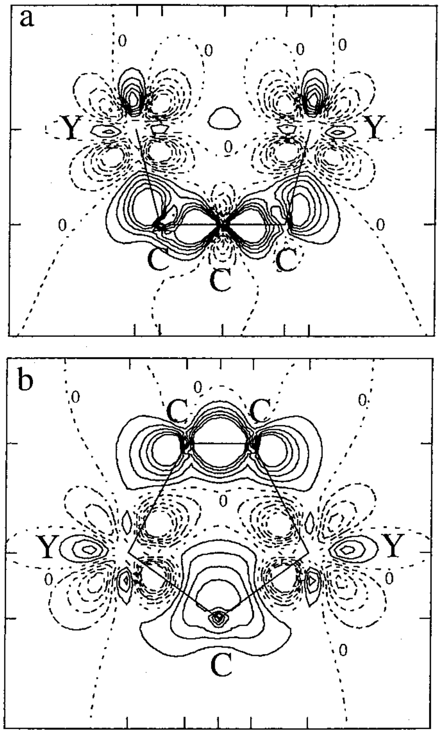

Figure 8. Electron density difference maps between Y_2C_3 and its atoms for open-C (a) and closed (b) structures. The spacing between the contours is 0.01 electron/bohr^3. The contours with no density change are labeled with zero. The solid lines indicate enhancement of electron density while the dotted lines represent depletion of electron density.

5. Computation of Thermodynamic Properties and Comparison with Experiment

The theoretical atomization energies were calculated for the computed ground states of Y_2C_n for the following process:

$$Y_2C_n(g) \rightarrow 2Y(g) + nC(g)$$

The atomization energies were computed for most state structures. In the case of Y_2C_2 (Figure 2), three structures were found to be suitable candidates for the ground state. Since interconversion among isomers would lead to breaking of bonds, all isomers can coexist. The computed enthalpies depend mainly on the quality of the electronic energy calculations. In general, the agreement with the experimental results is very good for the energies computed within the MP2 approach (Table 1).

Experimental results are also influenced by the structures of molecules which are needed for the third and second law calculations of the Gibbs free energy and heat content functions.

TABLE 1: Atomization Enthalpies for Diyttrium Carbides Y_2C_n ($n = 1-8$) (Energies in kJ/mol)[d]

species	DFT	MP2	exp[a]	exp (corr)[b]
Y_2C	788	829		
Y_2C_2	1414	1536	1587 ± 20	1549
Y_2C_3	2003	2057	2264 ± 20	2169
Y_2C_4	2718	2820	2993 ± 15	2940
Y_2C_5	3223	3301	3628 ± 20	3560
Y_2C_6	3820	4050[c]	4330 ± 20	4223
Y_2C_7	4424	4494[c]	4931 ± 45	4852
Y_2C_8	5103	5322[c]	5693 ± 40	

[a] Reference 18. [b] Results from ref 18 corrected for theoretical ground-state structures. [c] The MP2 energy was calculated for the DFT optimized structure. [d] The most stable structure was chosen for the computation of the atomization enthalpies.

In the absence of spectroscopic data for yttrium carbides, the thermodynamic properties were estimated from the assumed molecular parameters.[18] Table 2 presents the Gibbs free energy and heat content functions calculated for the computed ground state and the experimentally estimated values.[18] As can be seen from Table 2, the values of thermodynamic functions are less sensitive to the molecular structures than the electronic energies. Moreover, the experimentally estimated thermodynamic functions can be corrected for the assumed erroneous molecular structures as

$$\Delta = -T(\mathrm{GEF}_{\mathrm{est}} - \mathrm{GEF}_{\mathrm{calc}})$$

which gives corrections to the atomization energies calculated using the third law method. The detailed third law evaluations of the reaction enthalpies for Y_2C_n are available.[18] The theoretical GEF were calculated for sets of temperatures chosen from the experimental data, and the averaged correction (ΔE) was applied to the experimental results (Table 1). The correction narrows the difference between the experimental and theoretical evaluations. The zero-point vibrational energy correction lowers the calculated atomization enthalpies by 8.5 kJ/mol for Y_2C to 99.6 kJ/mol in the case of Y_2C_8.

6. Discussion and Conclusions

Although there are several experimental studies on transition dimetal carbides, theoretical work is restricted to $YIrC_n$ ($n = 1, 2$).[17] The current theoretical study presents systematic data on the molecular structures and energetics and the nature of bonding in Y_2C_n carbides for $n = 2-8$.

In contrast to pure carbon clusters, which are linear for $n < 10$, the ground-state isomers of diyttrium carbides exhibit cyclic structures. The atomic radius of yttrium is twice that of carbon, and thus the metal significantly enlarges the ring. Also, the 4d orbitals of Y are more flexible toward the formation of nonlinear bonds. However, the carbon chains within closed structures remain almost linear. Open structures are linear or have a C-shape. The carbon skeleton in the C-structures remains nearly linear. Due to symmetry breaking, the linear singlet state is always accompanied by a distorted (C-shape) triplet. The singlet state of the C-structure is coupled with a linear triplet.

The Y−C bonds are strongly ionic due to the transfer of an electron from Y to the carbon chains in the case of cyclic isomers, and about 0.5 electron transferred in open isomers. The spin multiplicity of the electronic state (singlet or triplet) under consideration has little impact on the amount of electronic transfer. The theoretically computed atomization energies of the ground-state structures are found to be in good agreement with the experimental atomization energies of Y_2C_n. The calculated enthalpies are sensitive to the inclusion of correlation energy, and the MP2 method gives better results than the ones obtained at the DFT level of theory in all cases studied here. A similar feature was noted for the YC_n species studied before.[14] Using the theoretically computed equilibrium structures and the partition functions, the experimental enthalpies[18] have been corrected for the assumed incorrect geometries. In all cases,

TABLE 2: Gibbs Energy Functions, GEF = $(G^0_T - H^0_T)/T$, and Heat Content Functions, $\Delta H = H^0_T - H^0_0$, Calculated for $n = 1-8$ of Y_2C_n within the Density Functional Formalism (GEF in J/mol, ΔH in kJ/mol)

			temp, K				
species	method		298	2400	2600	2800	3000
Y_2C	DFT	GEF	−259.9	−362.6	−367.0	−371.1	−388.8
		ΔH	12.4	131.7	143.3	154.9	124.6
Y_2C_2	DFT	GEF	−256.5	−400.9	−407.1	−412.8	−418.2
		ΔH	17.9	184.4	200.8	217.3	233.8
	EST[a]	GEF	−250.82	−386.53	−392.87	−398.78	−404.33
		ΔH	13.922	189.27	206.71	224.17	241.66
Y_2C_3	DFT	GEF	−298.7	−460.6	−468.6	−476.1	−483.2
		ΔH	15.3	240.6	262.7	285.0	307.2
	EST[a]	GEF	−262.59	−425.53	−433.45	−440.83	−447.78
		ΔH	15.873	236.14	258.43	280.76	303.14
Y_2C_4	DFT	GEF	−293.2	−485.0	−493.9	−502.2	−510.0
		ΔH	20.2	266.0	290.7	315.3	340.0
	EST[a]	GEF	*b*	−464.49	−473.98	−482.88	−491.22
		ΔH	17.828	283.02	310.15	337.36	364.63
Y_2C_5	DFT	GEF	−307.3	−529.4	−539.9	−549.8	−559.0
		ΔH	22.9	314.8	344.3	373.8	403.5
	EST[a]	GEF	−286.04	−503.49	−514.55	−524.93	−534.65
		ΔH	19.792	329.90	361.89	393.97	426.13
Y_2C_6	DFT	GEF	−323.0	−578.8	−591.5	−603.3	−614.4
		ΔH	24.4	377.1	413.1	449.2	485.4
	EST[a]	GEF	−297.74	−524.44	−555.07	−566.94	−578.13
		ΔH	21.760	376.79	413.63	450.59	487.65
Y_2C_7	DFT	GEF	−328.5	−609.4	−623.2	−636.1	−648.2
		ΔH	27.3	411.0	450.3	489.6	529.0
	EST[a]	GEF	−309.44	−581.40	−595.64	−608.98	−621.56
		ΔH	23.732	423.69	465.38	507.20	549.12

[a] From ref 18. [b] Value −156.46 in ref 18 is probably a misprint.

the corrected experimental energies were found to be closer to the computed values.

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