

# Isomeric C<sub>60</sub>F<sub>36</sub>(g) species: computed structures and heats of formation

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The recently measured heat of formation  $\Delta H_f^o$  of C<sub>60</sub>F<sub>36</sub>(g) is submitted to extensive computational treatment. The computations have been performed at the AM1, PM3 and SAM1 semiempirical quantum-chemical levels on a set of selected isomers, especially of *T*, *C*<sub>3</sub>, and *D*<sub>3d</sub> symmetries. The SAM1 method produces somewhat lower values than PM3 and especially AM1 (as it also does for pristine fullerenes). For example, the *T* isomer has the SAM1 computed value of  $-1293$  kcal/mol, i.e., within the experimental error bars. However, the issue of isomerism should also be taken into consideration accordingly, and related kinetic aspects should be checked by the computations. Even before those two additional steps are carried out, agreement between the observed and computed values is encouraging.

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At present, there are only four neutral fullerene species with measured [1–6] heats of formation  $\Delta H_f^o$ : C<sub>60</sub>, C<sub>70</sub>, C<sub>60</sub>F<sub>48</sub>, and, most recently [7], C<sub>60</sub>F<sub>36</sub>. The thermochemical data for fullerenes are relatively very rare owing to usually small amount of the available samples. Some thermochemical information can also be derived for gas-phase charged species [8] using the Knudsen cell mass spectrometry method. C<sub>60</sub>F<sub>36</sub> is rather well characterized experimentally as <sup>19</sup>F NMR spectra of its two isomers, *T* and *C*<sub>3</sub>, are available [9] (*T* and *C*<sub>3</sub> isomeric ratio is about 1 : 3). Clearly enough, the thermochemical measurements [7] on C<sub>60</sub>F<sub>36</sub> represent an important addition to the fullerene data (in the gaseous state at room temperature the experimental value reads  $\Delta H_{f,298}^o = -1248 \pm 48$  kcal/mol). In order to check the capability of computational tools, the heat of formation  $\Delta H_{f,298}^o$  is computed in this paper by means of semiempirical methods of quantum chemistry for several selected isomers of C<sub>60</sub>F<sub>36</sub>(g).

## 1. Computations

The full geometry optimizations were performed with the three key semiempirical methods that generally produce quantitative values of heats of formation: AM1 [10], PM3 [11], and SAM1 [12]. The SAM1 (Semi-Ab-Initio Model 1) method is the newest semiempirical quantum-chemical procedure, constructed [12] in order to fix some deficiencies of the previous approximations. The computations were carried out primarily with the SPARTAN [13] and AMPAC [14] program packages. The geometry optimizations were performed with no symmetry constraints in Cartesian coordinates and with analytically constructed energy gradient.

The full geometry optimizations were followed by the harmonic vibrational analysis in each of the three methods. The harmonic vibrational analysis was carried out by a

numerical differentiation of the analytical energy gradient. The computed vibrational eigenvalues are analyzed for presence of an imaginary frequency so that local minima and possible saddle points can be distinguished. Special attention has been paid to evaluation of the symmetries of the relaxed structures. Symmetry of the optimized structures was determined not only by the AMPAC built-in procedure [14], but primarily by a new, flexible one [15].

## 2. Results and discussion

We have been computing a set of isomers of C<sub>60</sub>F<sub>36</sub> with higher symmetries [16] like *T*, *D*<sub>3d</sub>, *T*<sub>h</sub>, *C*<sub>3</sub>, *C*<sub>2v</sub>. However, in this report we present results only for four isomers that have been found as the energy-lowest structures in the PM3 method in a preliminary search: *T*, *D*<sub>3d</sub>, *T*<sub>h</sub>, and *C*<sub>3</sub>.

The *T* isomer comes as the lowest-energy structure in all the three considered semiempirical methods (Table). In fact, the order of isomers is the same in the AM1 and PM3 methods but differs in the SAM1 method. The AM1 method has been known [17–19] to overestimate the heats of formation for the pristine species more than the PM3 method does. Table suggests that this is likely to remain true for fullerene fluoro-derivatives, too. On the other hand, the SAM1 method gives the  $\Delta H_{f,298}^o$  terms actually closer [18,19] to the observed values for the pristine fullerenes than the PM3 treatment. This is also seen in Table for C<sub>60</sub>F<sub>36</sub> as the SAM1  $\Delta H_{f,298}^o$  values basically coincide with the observed value [7] of  $-1248$  kcal/mol (if considered within its error bars of  $\pm 48$  kcal/mol). At present, it is still difficult to compute the total values of heats of formation *ab initio* unless some empirical terms are introduced. On the other hand, the separation energies between isomers can be computed by both semiempirical and nonempirical methods. The separation energies from both treatments usually agree well.

The AM1, PM3, and SAM1 heats of formation  $\Delta H_{f,298}^{\circ}$  for selected  $C_{60}F_{36}$  isomers

Species	$\Delta H_{f,298}^{\circ}$ , kcal/mol		
	AM1	PM3	SAM1
$C_3$	-889.68	-1079.52	-1228.94
$T_h$	-898.03	-1086.39	-1175.95
$D_{3d}$	-924.32	-1112.69	-1226.79
$T$	-952.76	-1134.27	-1292.97

Gas phase species throughout; the standard state - an ideal gas phase at 1 atm = 101 325 Pa pressure.

There is however a substantial qualitative difference seen in Table that the SAM1 order of structures is not exactly the same as those produced by the AM1 and PM3 methods. Once again, the SAM1 method is closer to the observed facts [7,9] as the structures seen in the experiment are of  $C_3$  and  $T$  symmetries. In fact, there are two  $C_3$  species considered in paper [9] as there is no direct way how to distinguish these two  $C_3$  isomers with the presently available data. The SAM1 method places the selected [9]  $C_3$  species as the second lowest in energy.

There is still one problem with the SAM1 results as the ratio of the  $C_3$  and  $T$  isomers is observed [9] as about 3 : 1. Hence, it is important to perform the computational evaluation of entropy effects according to the statistical-mechanical treatment [20] based on the quantum-chemical computations. It has been known for isomeric higher fullerenes [21] that the most abundant species is not necessarily the lowest-energy structure. This interesting fact is produced by entropy effects at higher temperatures.  $C_{60}F_{36}$  is indeed prepared [9] at temperatures around 350°C.

In overall, the reported quantum-chemical semiempirical computations point out the SAM1 method as the best applicable treatment that could well reproduce the experimental thermochemical data [7]. The final conclusion should be supported by entropy evaluations and also by some *ab initio* calculations or even by kinetic evaluations, these advanced topics being in progress in the lab.

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