

Small Molecules in C<sub>60</sub> and C<sub>70</sub>: Which Complexes Could Be Stabilized?Tatiana Korona<sup>\*,†</sup> and Helena Dodziuk<sup>\*,§</sup><sup>†</sup>Faculty of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland<sup>§</sup>Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44, 01-224 Warsaw, Poland

**ABSTRACT:** The recent syntheses of complexes involving some small molecules in opened fullerenes and those of hydrogen molecule(s) in C<sub>60</sub> and C<sub>70</sub> are accompanied in the literature by numerous computations for endohedral fullerene complexes which cope with the problem of the stability of these complexes. In this contribution, stabilization energies of endohedral complexes of C<sub>60</sub> and C<sub>70</sub> with H<sub>2</sub>, N<sub>2</sub>, CO, HCN, H<sub>2</sub>O, H<sub>2</sub>S, NH<sub>3</sub>, CH<sub>4</sub>, CO<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>, H<sub>2</sub>CO, and CH<sub>3</sub>OH guests have been estimated using symmetry-adapted perturbation theory, which, contrary to the standard DFT and some other approaches, correctly describes the dispersion contribution of the host–guest interactions. On the basis of these calculations, the endohedral complexes with all these guests were found stable in the larger fullerene, while the C<sub>60</sub> cage was found too small to host the latter four molecules. Except for H<sub>2</sub> and H<sub>2</sub>CO, a stabilization effect for most guests in the C<sub>60</sub> cage is about 30 kJ/mol. For H<sub>2</sub> and H<sub>2</sub>O guests, a typical supramolecular effect is observed; namely, the stabilization in the smaller cage is equal to or larger than that in the larger C<sub>70</sub> host. Except for the water molecule where the induction interaction plays a non-negligible role, in all complexes the main stabilization effect comes from the dispersion interaction. The information on the stability of hypothetical endohedral fullerene complexes and physical factors contributing to it can be of importance in designing future experiments contributing to their applications.

## ■ INTRODUCTION

The captivating idea of an empty space inside the C<sub>60</sub> cage that could be filled with atoms or molecules has been recognized from the early stages of fullerene study.<sup>1</sup> It was also soon realized that the confinement of a guest inside the fullerene cage would influence both host and guest<sup>2</sup> and could lead to various applications,<sup>2,3</sup> although most of them proved until now unrealizable.<sup>4</sup> Fullerenes can be used in medicine,<sup>5–7</sup> in photovoltaic devices,<sup>8,9</sup> and in electronics,<sup>10–12</sup> in particular, as single-molecule transistors for quantum computing.<sup>13–16</sup> Of special interest are so-called peapods formed by carbon nanotubes filled with endohedral fullerene complexes such as <sup>15</sup>N@C<sub>60</sub> or <sup>31</sup>P@C<sub>60</sub>, which are considered as promising elements of quantum-processing architecture.<sup>17</sup> In view of exciting properties and the prospects of applications, a prediction of stability and properties of endohedral fullerene complexes on the basis of computations seems to be quite important. In particular, the question of how many hydrogen molecules can be hosted by C<sub>60</sub> has drawn the attention of many researchers.<sup>18,19</sup> The published theoretical estimations vary from 1 to over 20, while only one H<sub>2</sub> molecule could be inserted in C<sub>60</sub>,<sup>20</sup> and in the synthesized mixture of H<sub>2</sub>@C<sub>70</sub> and 2H<sub>2</sub>@C<sub>70</sub>,<sup>21</sup> the latter complex was present as only a 4% admixture, which agrees well with the results obtained on the basis of a simplified model.<sup>22</sup> An often neglected fact that endohedral fullerene complexes are objects with distinct topological properties is worth mentioning.<sup>19,23</sup>

Fullerene endohedral complexes involving lanthanoide guests are probably the most studied, but recent syntheses of H<sub>2</sub>@C<sub>60</sub><sup>20</sup> and of a mixture of H<sub>2</sub>@C<sub>70</sub> and 2H<sub>2</sub>@C<sub>70</sub><sup>21</sup> using a “molecular surgery” approach consisting of the chemical opening of the cage, inserting the guest, and chemically closing the cage hole have paved the way to endohedral fullerenes with other guest molecules. Several open cage fullerenes with nonpolar or slightly polar molecular guests inserted have been reported. In addition

to H<sub>2</sub> in opened C<sub>60</sub>,<sup>20,24</sup> they include H<sub>2</sub>@C<sub>70</sub> and 2H<sub>2</sub>@C<sub>70</sub>,<sup>25</sup> N<sub>2</sub>,<sup>26</sup> H<sub>2</sub>O,<sup>27,28</sup> NH<sub>3</sub>,<sup>29</sup> CO,<sup>30</sup> and CH<sub>4</sub><sup>31</sup> in opened C<sub>60</sub>, CO@C<sub>60</sub>, and N<sub>2</sub> in C<sub>60</sub> and C<sub>70</sub>.<sup>32</sup> This vivid activity of synthetic chemists inspired us to analyze the stability of several endohedral fullerene complexes with small guest molecules.

It should be stressed that the calculations of endohedral fullerene complexes present a difficult task since, on the one hand, the systems under study are large and, on the other, weak dispersive interactions stabilizing the complexes with nonpolar or slightly polar guests are poorly described at low-level quantum chemical calculations tractable for such large systems. Earlier studies on endohedral fullerene complexes were summarized in two reviews.<sup>18,19</sup> A detailed discussion of published experimental and calculated data on endohedral fullerene complexes involving hydrogen guests has been published recently,<sup>33</sup> applying symmetry-adapted perturbation theory (SAPT)<sup>34,35</sup> on H<sub>2</sub>@C<sub>60</sub>, 2H<sub>2</sub>@C<sub>60</sub>, and 2H<sub>2</sub>@C<sub>70</sub>. Therefore, here, only new results for these complexes and those involving complexes with other nonpolar or slightly polar guests will be briefly discussed.

Endohedral complexes with C<sub>60</sub>, C<sub>70</sub>, two isomers of C<sub>76</sub>, seven isomers of C<sub>80</sub>, and nine isomers of C<sub>82</sub> with a series of nonpolar or slightly polar guest molecules were analyzed by Dodziuk et al.<sup>36</sup> using molecular mechanics (MM) calculations using two different force fields. The most interesting conclusion from these calculations (the qualitative results did not depend on the force field applied) was that only H<sub>2</sub>, H<sub>2</sub>O, and, possibly, NH<sub>3</sub> were stabilized inside C<sub>60</sub>. Thus, if endohedral fullerenes were to be applied (one of the potential applications envisaged by Stoddart<sup>3</sup> is their utilization as drug carriers), then the development of methods for production and purification of higher fullerenes was a must. Next, after learning about obtaining H<sub>2</sub>

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in  $C_{60}$  and two hydrogen molecules in opened  $C_{70}$ ,<sup>37</sup> Dodziuk et al. carried out MM calculations for 1–4  $H_2$  in  $C_{60}$ ,  $C_{70}$ , two isomers of  $C_{76}$ , two isomers of  $C_{78}$ , and seven isomers of  $C_{80}$ , finding that one guest molecule is stabilized in both  $C_{60}$  and  $C_{70}$ .<sup>36</sup> Although two  $H_2$ 's were also found stabilized in the latter host, the absolute value of stabilization energy was smaller by 1.8 kcal/mol than that of the  $H_2@C_{70}$  complex.<sup>22</sup> This effect is due to repulsion of two hydrogen molecules inside  $2H_2@C_{70}$ .

The conclusions of these studies were that (a) it would be difficult to close the  $C_{70}$  cage with two hydrogen molecules inside and (b)  $C_{80}$  or larger fullerene would be necessary to host three  $H_2$ 's. The former conclusion proved valid, and interestingly and somewhat accidentally, the experimental  $H_2@C_{70}:2H_2@C_{70}$  rate of 96:4<sup>21</sup> corresponded to the calculated energy difference. Extensive calculations for  $H_2$  and  $N_2$  in  $C_{60}$  at fixed geometries were carried out by Slanina et al., who utilized second-order Møller–Plesset (MP2), spin-component-scaled MP2 (SCS-MP2)<sup>38</sup> theories, and density functional theory (DFT) with the MPWB1K functional,<sup>39</sup> yielding the best estimates for the stabilization effect of 4 and 9 kcal/mol, respectively.<sup>40</sup> Ren and co-workers reported calculations for  $H_2$  inside the  $C_{60}$  cage, but their choice of methods—a combined PM3 and DFT study—has not been appropriate for such types of complexes, which are mainly bound by dispersion interactions.<sup>41</sup> One and two  $H_2$  molecules in  $C_{60}$  and two of them in  $C_{70}$  were calculated in our group<sup>33</sup> using SAPT(DFT) (SAPT with interacting molecules described on the DFT level), yielding one  $H_2$  stabilized in  $C_{60}$  and two of them in  $C_{70}$ . On the other hand, on the basis of calculations for the structures optimized at the PBE-D/def2-TZVPP level using several DFT functionals and MP2 and SCS-MP2 methods, Kruse and Grimme claimed that  $2H_2@C_{70}$  is more stable than  $H_2@C_{70}$ .<sup>42</sup> They even stated that we have obtained the same trend, although we have not considered the complex  $H_2@C_{70}$  explicitly.<sup>33</sup> In the interesting work of Sebastianelli et al.,<sup>43</sup> it was found that the translation–rotation zero-point energies constitute significant factors destabilizing the  $2H_2@C_{60}$  and  $3H_2@C_{70}$  complexes. The conclusions from their work should equally apply to other endohedral complexes, meaning, e.g., that even if the interaction energy for some fullerene complexes has been found negative, it does not automatically signify that the complex can be formed if too large zero-point translation and rotation motions are present. In a similar spirit, Yagi and Watanabe proposed to separate slow vibrational motions of a host within a new method called instantaneous vibrational analysis (IVA) and applied the new approach to study translational and rotational movement of water molecule inside the  $C_{60}$  cage.<sup>44</sup> They have found a considerable blue shift of vibrational levels of most configurations of water inside  $C_{60}$  and also noticed a significant dependence of the final results on the level of theory used to evaluate the potential for IVA. Recently, Min et al. studied the IR absorption of endohedral  $H_2$  in  $C_{60}$  in a wide range of temperatures, from 6 to 300 K.<sup>45</sup>

Several studies for complexes involving molecular guests other than hydrogen have been carried out. Unfortunately, most of them employed the computational methods, like standard DFT or semiempirical models, which are known to give unreliable results when utilized for nonpolar or slightly polar guests. The lack of a proper description of dispersion interactions in DFT with standard functionals makes all conclusions about endothermal effects involved in the complexation questionable at best. Utilizing extremely small basis sets is another common drawback of many fullerene studies. Although it is often difficult to afford

larger basis sets, an examination of rather subtle intermolecular interactions with inappropriate basis sets is of very limited significance. Therefore, such studies involving, e.g., geometry optimizations, should be at best accompanied with *a posteriori* single-point calculations for selected configurations, employing a more advanced method for describing electron correlation, like MP2 or SCS-MP2. In many cases, the stabilization only is achieved after the dispersion effect is taken into account. However, one should be aware that MP2 often overestimates the binding energy for the interacting molecules involving aromatic rings.<sup>46</sup> Some examples of such combined studies are given in works of Charkin et al., who performed a study on methane inside the  $C_{60}$  and  $C_{84}$  ( $T_d$ ) cages<sup>47</sup> and carbon dioxide, ethyne, and several other small molecules in the  $C_{70}$  cage<sup>48</sup> with the B3LYP functional and the 6-31G and 6-31G\* basis sets, followed by the MP2 computation used to obtain the dissociation energies. The same group calculated the properties of benzene and borazole inside the  $C_{84}$  fullerene.<sup>49</sup> Yet another application of this type has been reported by Slanina et al. for the nitrogen molecule in  $C_{60}$ .<sup>40,50</sup> The complexes of methane in  $C_{84}$  and  $C_{60}$  have also been calculated by Rehaman and co-workers.<sup>51</sup> However, only for the smaller host has the MP2 stabilization energy been reported, while for the  $CH_4@C_{84}$ , only the DFT value has been given. DFT calculations of Jin and co-workers on the complexes of  $C_2H_2@C_{60}$ ,  $C_2H_4@C_{60}$ , and  $C_2H_6@C_{60}$ <sup>52</sup> also seem of too low accuracy to yield reliable results. Some GGA functionals have been applied by Gao et al.<sup>53</sup> to  $N_2@C_{60}$ , in which a considerable interaction of the lone pairs on nitrogen atoms with the  $\pi$  electrons of the cage can be expected. Therefore, the conclusion of Gao and co-workers on the small effect of the guest inclusion on the properties of the complex is questionable. Another example of an inappropriate choice of methodology is the work by Mazurek and Sadlej-Sosnowska,<sup>54</sup> who utilized very small basis sets for the Hartree–Fock (HF), DFT, and MP2 calculations of the complex of benzene enclathrated inside  $C_{60}$ . Therefore, their conclusion that such a complex would be stable cannot be trusted. Note that it can be easily seen that the distances between guest hydrogen atoms and host carbon atoms are considerably smaller than the sum of their van der Waals radii; therefore, large repulsion effects should be expected.

Ren and co-workers<sup>55</sup> performed B3LYP/6-31G(d) calculations for the hypothetical highly reactive tetrahedrane inside  $C_{60}$ . Although the effect of stabilization of a short-lived species in a fullerene cage has been already reported (see the discussion by Dodziuk)<sup>56</sup> and the cyclobutadiene synthesis inside a hemispherical cage has been executed by the Cram group,<sup>57</sup> for the case investigated by the Ren group, there is no way to insert a short-lived tetrahedrane into the fullerene cage to allow one to test its stabilization. Similarly, obtaining hypercoordinated cluster  $C_2$  inside highly unstable  $C_{20}$  and  $C_{24}$ , for which Wang et al.<sup>58</sup> reported the DFT calculations, seems hardly possible, although the synthesis of the former cage has been achieved.<sup>59</sup>

In another study, Hu and Ruckenstein<sup>60</sup> reported HF calculations for  $H_2$  and CO molecules inside the  $C_{58}$  cage with a seven-membered ring. It is, however, well-known from the early Cioslowski calculations<sup>61</sup> that the HF method is not capable of describing the stabilization of endohedral fullerene complexes with a nonpolar or slightly polar guest, due to the lack of dispersion interactions (note, however, that Cioslowski did not draw this conclusion in the paper).<sup>61</sup> The DFT calculations for the hypothetical saturated  $C_{60}H_{60}$  cage with small guest molecules have been reported by Hu and Ruckenstein.<sup>62</sup> However,

the cage has been shown by Saunders<sup>63</sup> and Dodziuk and Nowiński<sup>64</sup> to be highly strained if all CH bonds point outside. Therefore, the investigations by Hu and Ruckenstein have a very limited foreseeable value. The former authors also carried out HF and B3LYP calculations for the opened C<sub>60</sub> cage which are indispensable for the manufacturing of endohedral fullerene complexes with nonpolar or slightly polar molecules.<sup>60</sup> Unfortunately, also here the selection of the computational methods put in doubt the reliability of the results obtained.

In this study, we want to present the calculations of the stabilization energies of endohedral complexes of the C<sub>60</sub> and C<sub>70</sub> fullerenes with several small guest molecules, performed using the accurate SAPT approach. This method, although more demanding in terms of the computational resources than the supermolecular HF and DFT methods, yields in return very reliable results, which for small molecules compare favorably to those obtained by the highly accurate supermolecular CCSD(T) method.<sup>65,66</sup> With increasing computer power, this method has become affordable and easy to use, even for the fullerene complexes, and can therefore allow one to evaluate the quality of other methods, utilized so far for systems of such sizes.<sup>33,67–70</sup> A separation of energy components into physically sound contributions allows us additionally to analyze the sources of stability or instability of a given endohedral complex under scrutiny. As mentioned above, several uses of the endohedral fullerene complexes have been proposed but not yet implemented. We believe that a better understanding of forces stabilizing the complexes can contribute to the development of their marketable applications.

## METHOD

The interaction energy of two molecules A and B is conveniently defined as a difference of the energy of the inclusion complex and the sum of energies of constituent molecules:

$$E_{\text{int}} = E(A@B) - [E(A) + E(B)] \quad (1)$$

Note that in this definition the geometries of A and B do not change in the complex. The stabilization energy is then defined as the interaction energy calculated at a minimum. Two approaches are applied to calculate this energy: the supermolecular and the perturbational ones. In the first approach, the definition (eq 1) is directly used to calculate the interaction energy, where the energies of A@B, A, and B are obtained from the computational quantum chemistry method, like, e.g., CCSD(T), MP2, HF, or DFT. The supermolecular approach is easy to utilize, but one should be aware of the limitations of the methods used to obtain  $E(A@B)$ ,  $E(A)$ , and  $E(B)$  so that no important components of the interaction energy are lost (like the dispersion energy, which is absent in the supermolecular HF interaction energy).

In the second approach, the interaction energy is derived from perturbation theory with the intermolecular interaction operator being the perturbation operator and with the sum of Hamiltonians of molecules A and B being the unperturbed operator. The most successful perturbational theory applied to the intermolecular interactions is the approach proposed and developed by Jeziorski et al., which bears the name symmetry-adapted perturbation theory (SAPT).<sup>34,35</sup> Since we do not know the exact wave functions for the unperturbed molecules A and B, which is usually a prerequisite of employing the perturbational method, several approaches have been developed to cope with this problem, among which the description of the interacting molecules on the

DFT level is the only practical way to treat large complexes, especially if two-electron repulsion integrals are calculated with help of the density-fitting (DF) technique<sup>71</sup> (see, e.g., refs 65, 72–76).

The idea of applying DFT in SAPT is a successful example of “taking the best from both worlds”, i.e., treating the intramolecular electron correlation by DFT and the intermolecular (i.e., the dispersion effect) by the *ab initio* perturbational method. The quality of the SAPT(DFT) (called alternatively DFT-SAPT) approach has been critically evaluated by comparing it with the supermolecular CCSD(T) results<sup>65,66</sup> and recently with accurate SAPT(CCSD) calculations (see, e.g., refs 77–79). The results of this comparison confirm that the SAPT(DFT) usually reproduces quite accurately the so-called intramonomer electron-correlation effects and that it is therefore the best possible method up-to-date capable of treating large van der Waals complexes.

In SAPT, the interaction energy is obtained as a sum of several physically sound energy contributions, i.e., the electrostatic, induction, and dispersion energies and their exchange counterparts, which arise from the imposition of the Pauli exclusion principle on the approximate wave function

$$E_{\text{int}} = E_{\text{elst}}^{(1)} + E_{\text{exch}}^{(1)} + E_{\text{ind}}^{(2)} + E_{\text{exch-ind}}^{(2)} + E_{\text{disp}}^{(2)} + E_{\text{exch-disp}}^{(2)} \quad (2)$$

Therefore, SAPT not only provides us the total interaction energy, like the supermolecular methods do, but additionally, it allows for an analysis of the importance of various contributions to the interaction energy. It should be noted parenthetically that in SAPT the intermolecular interaction operator is utilized in an exact, nonexpanded form; i.e., no multipole expansion is employed, thus avoiding possible complications arising from the divergent character of the inverse-distance series. It should be emphasized that for the case of the endohedral complex the usual expanded form of the interaction potential cannot be utilized at all. If for some reason the expanded form of the potential is necessary, the form presented in refs 80 and 81 should be applied.

In this work, DF-DFT-SAPT (i.e., DFT-SAPT with two-electron repulsion integrals calculated with help of the DF technique) implemented in the Molpro suite of programs<sup>82</sup> has been used to calculate the stabilization energies of the complexes. The interacting molecules in DFT-SAPT have been described by the PBE functional,<sup>83</sup> with the asymptotic correction as proposed in ref 84. For a calculation of this correction, we took the experimental ionization potentials from refs 85 and 86 for C<sub>60</sub> and C<sub>70</sub>, respectively, or from the Web site <http://cccbdb.nist.gov/exp2.asp> for other molecules, while the DFT HOMO energies have been calculated in the same basis as used in DFT-SAPT.

The geometries of the complexes were prepared using molecular mechanics with the MM3<sup>87–89</sup> parametrization. The minimized structures were then reoptimized using the ArgusLab package (<http://www.arguslab.com/>) with the PM3 method. Several input geometries have been tried in MM and (e.g., for the linear guests involving C<sub>60</sub>) the guest has been orientated perpendicular to the six- or five-membered rings of the host. The steric energy of the system has been minimized, whereas for C<sub>70</sub> complexes, three guest orientations for the starting geometry (along the long axis and perpendicular to it) have been minimized. Only the geometries corresponding to the lowest MM energies have been selected for the single-point DFT-SAPT calculations. We are aware that this method of selection of the configurations cannot locate the DFT-SAPT minimum exactly, but the full geometry optimization by a more advanced method,



**Table 1.** Calculated SAPT(DFT) Interaction Energies in the TZVP Basis Set for the Complexes of Linear, Planar, and Three-Dimensional Guests in C<sub>60</sub> and C<sub>70</sub> in kilojoules per mole<sup>a</sup>

guest	C <sub>60</sub> host	C <sub>70</sub> host
linear guests		
H <sub>2</sub>	−13.2 <sup>b</sup>	−13.0
N <sub>2</sub>	−15.9	−30.1
CO	−21.4	−31.2
HCN <sup>c</sup>	9.8	−40.2
HCN <sup>d</sup>	−6.3	not calculated
CO <sub>2</sub>	117.9	−32.2
C <sub>2</sub> H <sub>2</sub>	73.0	−22.2
planar guests		
H <sub>2</sub> O	−30.8	−27.9
H <sub>2</sub> S	−32.0	−33.1
H <sub>2</sub> CO <sup>c</sup>	65.1	1.8
H <sub>2</sub> CO <sup>d</sup>	not calculated	−8.6
nonplanar guests		
NH <sub>3</sub>	−22.6	−30.7
CH <sub>4</sub> <sup>c</sup>	−6.2	−23.8
CH <sub>4</sub> <sup>d</sup>	−16.5	not calculated
CH <sub>3</sub> OH	199.1	−29.7

<sup>a</sup>For a few cases, the calculations were repeated in the larger def2-TZVPP basis. <sup>b</sup>In ref 35, where the better TZVPP basis has been used for this complex, the interaction energy was equal to (−19.3) − (−19.4) kJ/mol for three orientations studied, while for one orientation (the hydrogen molecule parallel to one hexagon), it was higher by 0.76 kJ/mol. <sup>c</sup>Calculated using TZVP basis set. <sup>d</sup>Calculated using def2-TZVPP basis set.

like DFT (with a possible addition of dispersion correction by the Grimme method<sup>38</sup>) or MP2 in a reasonable basis, is beyond our computer capacities. Our previous studies on just one complex (H<sub>2</sub>@C<sub>60</sub>)<sup>78</sup> indicate that the potential energy surface is almost flat in the minimum region and that, e.g., moving the H<sub>2</sub> molecule by 0.2 Å from the center of the cage changes the interaction energy by only 0.3 kJ/mol. We have also performed some test calculations for an example of larger water guests in C<sub>60</sub> and changed the PM3 configuration by shifting H<sub>2</sub>O by 0.03 to 0.10 Å off the fullerene center or by elongating the O–H bonds by 1%. Such configuration modifications resulted in the energy lowering or raising by at most 0.25 kJ/mol. Therefore, it seems that locating the minimum by a very approximate method, like MM or PM3, should not change the general conclusions about values of the DFT-SAPT stabilization energies by more than a few tenths of kilojoule per mole.

Sizes of the complexes prevent us from utilizing large basis sets. To counterbalance the computational time and accuracy, we decided to employ the TZVP basis set<sup>90,91</sup> with the corresponding auxiliary basis sets for density-fitting.<sup>92,93</sup> In our previous work on hydrogen molecules in C<sub>60</sub>, we have checked that this basis set gives similar values of energy contributions to those of a larger TZVPP basis for all components, but for the dispersion energy, the TZVPP basis gave a 15% larger value. Since the main aim of the present calculations is to estimate the stability of various species, we can safely say that if the complex should be stable on the basis of the DFT-SAPT calculation in a smaller

TZVP basis, it will certainly be stable in any more elaborate basis. In several cases, when the stabilization energy in the TZVP basis set turns out to be close to zero, the calculations in the def2-TZVPP<sup>94</sup> basis set have been performed as well in order to verify whether the better basis set yields stabilization of the complexes. However, since the calculation of a single point with DF-DFT-SAPT in the TZVP basis set takes 2–3 days with available computer facilities, depending on the complex size, and becomes 2.5–3 times longer in the def2-TZVPP basis, we renounce the idea of recalculating all complexes under study in the larger basis.

## RESULTS AND DISCUSSION

The calculated interaction energies (see Table 1) obtained with the TZVP basis indicate that, except probably CH<sub>2</sub>O, all molecules under scrutiny are stabilized in the C<sub>70</sub> host, while HCN, CH<sub>2</sub>O, C<sub>2</sub>H<sub>2</sub>, CO<sub>2</sub>, and CH<sub>3</sub>OH do not form stable complexes in C<sub>60</sub>. Moreover, a rather small energy value for the CH<sub>4</sub>@C<sub>60</sub> complex suggests that its stability can be jeopardized if, in addition, the zero-point energies are included, which can be equal to a few kilojoules per mole (see refs 43–47). As mentioned above, in order to verify the stability of this complex, an additional calculation in the larger def2-TZVPP basis has been performed. In the new basis, the energy becomes lower by as much as 10 kJ/mol. This finding is mainly attributed to the improved description of the dispersion component of the interaction energy (see Table 2). Similarly, a repeated calculation for the CH<sub>2</sub>O@C<sub>70</sub> in the def2-TZVPP basis yields a small stabilization, which is mostly due to the improved description of the dispersion interactions. Therefore, for the case of a larger fullerene, the DF-DFT-SAPT method predicts that the endohedral complexes with all guests under study are stabilized.

For obvious reasons, for many pairs involving the same guest and different hosts, it can be observed that the stabilization is larger in the larger host. It is noteworthy that several complexes involving the latter cage (with N<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub>S, NH<sub>3</sub>, and CH<sub>3</sub>OH guests) exhibit very close values of the stabilization energy (−30 ± 3 kJ/mol). Actually, only the complexes H<sub>2</sub>@C<sub>70</sub> and H<sub>2</sub>CO@C<sub>70</sub> have a very different stabilization energy of −13 kJ/mol and 1.8 (or −8.6 in the larger basis) kJ/mol, respectively, while the largest absolute value of 40 kJ/mol has been found for the complex HCN@C<sub>70</sub>. However, the H<sub>2</sub> and, especially, H<sub>2</sub>O complexes in both fullerenes under consideration exhibit an effect typical for supramolecular chemistry. Namely, the absolute value of the stabilization energy in the smaller, in size, cage is equal to or even larger than that in the larger C<sub>70</sub> host. This effect can be rationalized by the fact that in a smaller cage more carbon atoms are close to the guest. Thus, and if the net interaction with the carbon atom is stabilizing, this results in a larger or equal stabilization of this guest in the smaller fullerene.

To analyze the factors influencing stabilization of the complexes, let us look at the SAPT components, which are shown in Table 2 for the fullerene C<sub>60</sub> and in Table 3 for the larger fullerene. First, it should be noted that for endohedral complexes it is inappropriate to think in terms of the usual asymptotic description of the energy components (e.g., interaction of dipoles etc.), since the interacting molecules are too close to one another. Thus, in this case, the short-range part of the components, i.e., the one resulting from the overlapping of the electron clouds, comes into play.

Starting from the first-order corrections, one can say that the electrostatic energy is relatively large (i.e., it constitutes a large

Table 2. SAPT Interactions Energy Components (in kJ/mol) for the Complexes with C<sub>60</sub><sup>a</sup>

	$E_{\text{elst}}^{(1)}$	$E_{\text{exch}}^{(1)}$	$E_{\text{ind}}^{(2)}$	$E_{\text{exch-ind}}^{(2)}$	$E_{\text{disp}}^{(2)}$	$E_{\text{exch-disp}}^{(2)}$	$E_1$	$E_2$	$E_{\text{int}}$	$E_{\text{int}}^d$
H <sub>2</sub>	−7.4	21.5	−4.9	4.5	−30.9	4.1	14.1	−27.3	−13.2	−16.3
N <sub>2</sub>	−18.1	51.4	−16.8	15.4	−55.1	7.4	33.3	−49.2	−15.9	−21.4
CO	−23.7	61.2	−27.8	24.1	−65.5	10.3	37.4	−58.8	−21.4	−28.0
HCN <sup>b</sup>	−91.1	233.0	−99.6	86.4	−151.2	32.5	141.9	−132.0	9.8	−5.3
HCN <sup>c</sup>	−90.4	234.2	−108.7	91.2	−165.7	33.1	143.8	−150.1	−6.3	
CO <sub>2</sub>	−168.7	450.7	−189.3	181.2	−202.6	46.6	282.0	−164.1	117.9	97.7
C <sub>2</sub> H <sub>2</sub>	−166.2	443.8	−220.9	187.8	−224.1	52.6	277.6	−204.5	73.0	50.6
H <sub>2</sub> O	−13.3	35.6	−18.3	10.7	−52.4	7.0	22.2	−53.0	−30.8	−36.0
H <sub>2</sub> S	−69.8	159.9	−92.3	83.6	−143.3	29.9	90.1	−122.1	−32.0	−46.3
H <sub>2</sub> CO	−147.9	369.2	−178.5	161.7	−181.7	42.3	221.3	−156.2	65.1	46.9
NH <sub>3</sub>	−62.7	149.2	−85.8	74.8	−124.3	26.2	86.5	−109.1	−22.6	−35.1
CH <sub>4</sub> <sup>b</sup>	−75.3	190.5	−83.0	78.4	−146.9	30.1	115.2	−121.4	−6.2	−20.9
CH <sub>4</sub> <sup>c</sup>	−74.2	190.6	−81.1	76.4	−159.3	31.3	116.4	−132.9	−16.5	
CH <sub>3</sub> OH	−269.1	712.0	−372.3	322.1	−262.5	68.9	442.9	−243.8	199.1	172.9

<sup>a</sup>  $E_1$  and  $E_2$  are the sums of the first-order and the second-order components, respectively. <sup>b</sup> Calculated using the TZVP basis set. <sup>c</sup> Calculated using the def2-TZVPP basis set. <sup>d</sup> Obtained by adding 10% of  $E_{\text{disp}}^{(2)}$  to  $E_{\text{int}}$  calculated in the TZVP basis

Table 3. SAPT Interaction Energy Components (in kJ/mol) for the Complexes with C<sub>70</sub><sup>a</sup>

	$E_{\text{elst}}^{(1)}$	$E_{\text{exch}}^{(1)}$	$E_{\text{ind}}^{(2)}$	$E_{\text{exch-ind}}^{(2)}$	$E_{\text{disp}}^{(2)}$	$E_{\text{exch-disp}}^{(2)}$	$E_1$	$E_2$	$E_{\text{int}}$	$E_{\text{int}}^d$
H <sub>2</sub>	−4.7	13.1	−2.8	2.5	−23.8	2.7	8.4	−21.4	−13.0	−15.4
N <sub>2</sub>	−23.7	63.5	−19.7	18.8	−79.6	10.4	39.8	−70.0	−30.1	−38.1
CO	−28.9	73.4	−26.4	25.0	−86.8	12.5	44.5	−75.6	−31.2	−39.8
HCN	−52.3	131.1	−64.4	53.9	−132.4	24.0	78.8	−118.8	−40.1	−53.3
CO <sub>2</sub>	−40.9	106.3	−37.0	34.2	−110.7	16.0	65.4	−97.6	−32.2	−43.2
C <sub>2</sub> H <sub>2</sub>	−63.8	167.1	−81.8	73.6	−145.5	28.1	103.3	−125.4	−22.2	−36.8
H <sub>2</sub> O	−12.1	35.0	−18.6	11.8	−51.0	7.1	22.9	−50.8	−27.9	−33.0
H <sub>2</sub> S	−66.3	151.4	−96.9	89.2	−139.7	29.3	85.0	−118.1	−33.1	−47.0
H <sub>2</sub> CO <sup>b</sup>	−63.5	163.4	−95.1	91.4	−118.0	23.5	100.0	−98.2	1.8	−10.0
H <sub>2</sub> CO <sup>c</sup>	−62.9	164.4	−72.9	67.6	−127.6	22.8	101.5	−110.1	−8.6	
NH <sub>3</sub>	−37.1	91.0	−54.2	46.3	−94.2	17.4	−84.7	−70.0	−30.7	−40.1
CH <sub>4</sub>	−43.8	114.9	−45.2	42.9	−112.0	19.4	71.1	−94.9	−23.8	−35.0
CH <sub>3</sub> OH	−69.0	177.3	−75.9	65.5	−155.7	28.0	108.3	−138.0	−29.7	−45.3

<sup>a</sup>  $E_1$  and  $E_2$  are the sums of the first-order and the second-order components, respectively. <sup>b</sup> Calculated using TZVP basis set. <sup>c</sup> Calculated using def2-TZVPP basis set. <sup>d</sup> Obtained by adding 10% of  $E_{\text{disp}}^{(2)}$  to  $E_{\text{int}}$  calculated in the TZVP basis

part of the total interaction energy) in all cases, but it is completely quenched by the first-order exchange term (coming from the Pauli exclusion principle), and that in all cases the net contribution from the interaction of the nonperturbed electron clouds of the host and guest is strongly repulsive (see the column with the total first-order energy, i.e., the  $E_1$  column). In addition, the amount of this repulsion is obviously dependent on the size of the guest. The examination of the pair of the second-order induction and exchange-induction energies reveals that in the majority of cases the positive exchange-induction term cancels the negative induction contribution, leaving a small negative stabilizing contribution. Such a behavior is characteristic for the interaction of highly symmetric molecules with one another and can be explained by the fact that the main component of the induction term comes in this case from the short-range effect, i.e., overlapping of the perturbed electron clouds. The notable exception is the water guest, in which case, almost a half of the induction contribution remains. For other polar molecules, the quenching is still big because even though they have sizable

dipole moments, their electron clouds overlap strongly with the host's cloud, creating a short-range induction component. However, one can see that for polar molecules some small, but non-negligible, net contribution remains. Importantly, in some cases, the latter is crucial to ensuring the negative interaction energy or at least make it less positive (as for CH<sub>3</sub>OH in C<sub>70</sub> and C<sub>60</sub>, respectively). Interestingly, for the methane molecule, the induction term contributes a lot to the negative interaction energy, although this molecule does not have a permanent dipole and quadrupole moment. The importance of the short-range induction contribution for the case of the methane molecule has also been observed in an investigation of the complex of Ar with CH<sub>4</sub> reported by Heijmen et al.<sup>95</sup>

The last pair of SAPT components, i.e., the second-order dispersion and exchange-dispersion energies, exhibits different behavior in comparison to the induction and exchange-induction pair. The exchange-dispersion energy never quenches the dispersion to a large extent. Quite on the contrary, it counterbalances at most 26% (usually 10–20%) of the dispersion effect. In this way,

the dispersion is the major negative contribution and is mainly responsive for binding of the guest inside the host. For smaller guests, its magnitude is sufficient to counterbalance the destabilizing effect of the first-order repulsion term, making the guest–host system stable.

In Tables 2 and 3, the interaction energies of two complexes,  $\text{HCN}@C_{60}$  and  $\text{H}_2\text{CO}@C_{70}$ , calculated in the TZVP basis set assume small positive values. As mentioned above, to check whether this destabilization could be due to the small basis set applied, additional calculations with the def2-TZVPP basis set were performed. As expected, the dispersion energy turned out to be the most sensitive to the quality of the basis set, and an addition of the polarization Gaussian functions resulted in lowering of both the dispersion energy and total interaction energy, leading to the stabilization of the complexes. The resulting increase in the absolute value of the dispersion contribution was about 10% of its value in a smaller basis. Since other components (see the electrostatic energy, first-order exchange energy, and the sum of the second-order induction and exchange-induction energies) are not that sensitive to the basis set effect, we decided to estimate the increase in the stabilization caused by the saturation of the dispersion components by scaling of the  $E_{\text{disp}}^{(2)}$  term by 10%. The resulting estimated interaction energy is given in the last column in Tables 2 and 3. Such a rescaling procedure has been already utilized in SAPT calculations in similar cases, i.e., when the application of the large basis was not possible because of the hardware limitations, and has been shown to substantially improve the quality of the potential energy surface.<sup>96</sup> It can be seen that—as expected—the stabilization of the complexes becomes larger with the rescaled dispersion, or (for some larger guest in the smaller cage) they become less destabilized. The effect is especially pronounced for nonpolar guests, in which case the dispersion is the main attractive component of the interaction energy. It is also interesting to note that for two isoelectronic guests of approximately the same size,  $\text{N}_2$  and  $\text{CO}$ , a difference of about 5 kJ/mol in the total energy appears. An inspection of data presented in Table 2 allows one to draw a conclusion that the nonsymmetric distribution of the electron density for  $\text{CO}$  causes a stronger interaction with the  $C_{60}$  cage. This effect for the unperturbed densities can be observed as larger absolute values of the electrostatic and first-order exchange energies. Similarly, the perturbed densities cause qualitatively the same effect for the induction and exchange-induction pair; i.e., charge redistribution in the cage caused by  $\text{CO}$  is larger than by  $\text{N}_2$ . Also, the dispersion and exchange-dispersion terms contribute to this effect, giving the net increase of the stabilization energy. Interestingly enough, the net stabilization energy for both species in the larger cage is virtually the same. However, the components are quite different (see Table 3).

Although the stabilization energy is the most popular and easy to obtain parameter of the stability of the endohedral complexes, an ultimate test of stability should be the thermodynamic functions, like enthalpies or Gibbs energies. However, in both cases, the calculation of the vibrational frequencies of the complex and the constituent molecules is necessary, which is quite expensive for a molecule of fullerenes' size. Therefore, such studies are much more rare. Slanina and Nagase<sup>50</sup> have obtained an estimate of the Gibbs energy for the  $\text{N}_2@C_{60}$  complex and have found that the entropic contribution is quite significant (the MP2 stabilization energy and the  $T\Delta S$  value are equal to  $-9.8$  kcal/mol and  $-5.9$  kcal/mol, respectively), although the

stabilization effect prevails. On the basis of this study, one can estimate that some of the complexes studied by us can be thermodynamically unstable at room temperature. However, due to the high energy of CC bond breaking, once formed, they can be, like cubane, kinetically stable. It should be also noted that the harmonic approximation, utilized almost exclusively to estimate the thermal contribution from the vibrations, could be insufficient for some modes of endohedral complexes.<sup>45</sup>

## SUMMARY

We performed the calculations of the stabilization energies of several endohedral complexes with  $C_{60}$  and  $C_{70}$  fullerenes with the recently developed DF-DFT-SAPT approach. On the basis of these results, the stability of all guests under study in the latter, larger fullerene is predicted, while larger guests, i.e.,  $\text{CO}_2$ ,  $\text{C}_2\text{H}_2$ ,  $\text{H}_2\text{CO}$ , and  $\text{CH}_3\text{OH}$ , are not stabilized in the  $C_{60}$  cage. However, a general conclusion of Dodziuk et al.<sup>36</sup> that mastering the manufacturing and purification of larger fullerenes is necessary for applications of their endohedral complexes with molecular guests remains in force. The analysis of the energy components reveals that the main stabilizing effect is always due to the dispersion energy, while the net contribution of the first-order terms is always repulsive. Only for the highly polar molecules does the induction effect of polarizing the cage by the electrostatic field of the guest contribute non-negligibly to the stabilization of the complexes. Taking into account that few small molecules have been found trapped in the opened  $C_{60}$ , we expect that the cages will be chemically closed in the near future, providing the corresponding endohedral complexes. At present, no devices on the basis of endohedral fullerene complexes are available on the market, in spite of numerous proposals of their applications. We believe that an understanding of forces stabilizing them can contribute to their development and practical use in the near future.

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