

## Chemical Bonding in the Inclusion Complex of He in Adamantane (He@adam): The Origin of the Barrier to Dissociation

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Four years ago we published the results of an extensive computational study of the structure and bonding in the inclusion complex of a He atom in an adamantane (C<sub>10</sub>H<sub>16</sub>) cage, He@adam, by density functional theory (DFT) calculations at the B3LYP/6-311++G(2d,2p) level.<sup>[1]</sup>

Structure optimization of the free adamantane molecule confirmed that the equilibrium structure has *T<sub>d</sub>* symmetry and yielded a C–C bond length of 154.0 pm and a <sup>1</sup>C–<sup>s</sup>C–<sup>1</sup>C valence angle of 109.7° (<sup>s</sup>C=secondary carbon atom, <sup>1</sup>C=tertiary carbon atom), both in excellent agreement with the experimental values, *r<sub>a</sub>*=154.0(2) pm and *θ<sub>a</sub>*=109.8(7)°, respectively.<sup>[2]</sup> Structure optimization of the He@adam complex showed that it retained the *T<sub>d</sub>* symmetry of the adamantane cage (see Figure 1). The distance from the He atom to the four tertiary carbon atoms (<sup>1</sup>C) was found to be 162.1 pm; the distance to the six secondary carbon atoms (<sup>s</sup>C) was 184.4 pm.

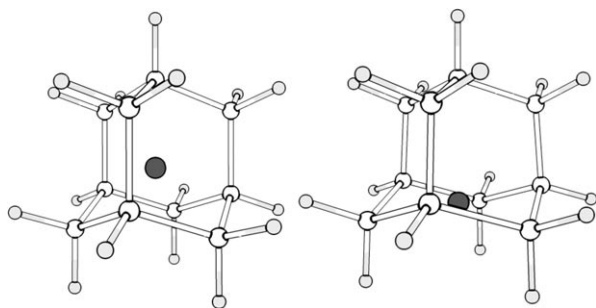


Figure 1. Left: the equilibrium structure of the endohedral complex He@adam. Right: the transition-state structure for the dissociation reaction, [He@adam]<sup>‡</sup>.

The sum of the van der Waals radii of a He atom (148 pm)<sup>[3]</sup> and of a spherically averaged methane molecule (201 pm)<sup>[4]</sup> suggests that He⋯C interactions should be strongly repulsive at distances shorter than 200 pm. Indeed, DFT calculations on the He⋯H<sub>3</sub>CH dimer optimized under *C<sub>3v</sub>* symmetry with He⋯C distances fixed at values ranging from 320 to 160 pm, showed that the interaction energy increase monotonically with decreasing distance and reach a value of 177 kJ mol<sup>-1</sup> at He⋯C=162.1 pm.<sup>[1]</sup>

The energy of formation of the complex, defined as the energy of the reaction given in Equation (1), was found to be large and positive [Eq. (2)]



$$\Delta E_f = E(\text{He@adam}) - E(\text{adam}) - E(\text{He}) = 645 \text{ kJ mol}^{-1} \quad (2)$$

Introduction of the He atom led to an elongation of the C–C bond length from 154.0 to 160.5 pm, while the <sup>1</sup>C–<sup>s</sup>C–<sup>1</sup>C valence angles opened to 111.1°. The large positive energy of formation and the marked elongation of the C–C bonds were interpreted as the result of strong repulsive He⋯<sup>1</sup>C interactions.

Formation of the complex [Eq. (1)] may be divided into two steps; the first involves the deformation of the adamantane cage to the structure adopted in the complex (*adam*<sup>\*</sup>), the second the introduction of the He atom into the preformed cage. The adamantane deformation (or strain) energy calculated for the first step is given in Equation (3). The He–adamantane interaction (or He⋯C repulsion) energy, calculated for the second step is given in Equation (4).

$$\Delta E_{\text{def}} = E(\text{adam}^*) - E(\text{adam}) = 64 \text{ kJ mol}^{-1} \quad (3)$$

$$\Delta E_{\text{int}} = E(\text{He@adam}) - E(\text{adam}^*) - E(\text{He}) = 581 \text{ kJ mol}^{-1} \quad (4)$$

The major part, about 90%, of the positive energy of formation is thus due to He⋯C repulsion.

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Alternatively, one may divide the formation reaction [Eq. (1)] into two steps in such a way that the first step involves the introduction of the He atom into a rigid adamantane cage of unchanging structure, and the second step the structural relaxation of the cage. The calculated energy of the first step is  $716 \text{ kJ mol}^{-1}$  and that of the second  $-71 \text{ kJ mol}^{-1}$ ; expansion of the cage reduces the large positive energy of formation. At the same time part of the energy of the complex is transferred from repulsive He...C interactions to strain energy of the cage.

Topological analysis by using the "Atoms in Molecules" (AIM) theory developed by Bader and co-workers<sup>[5]</sup> yields atomic interaction lines between the He atom and the four tertiary carbon atoms (<sup>1</sup>C), but not between He and the six secondary carbon atoms (<sup>2</sup>C). Assuming therefore that the He atom interacts primarily with the tertiary carbon atoms, the energy of formation corresponds to a positive mean He...<sup>1</sup>C interaction energy of  $161 \text{ kJ mol}^{-1}$ , that is, very similar to the interaction energy of the He...H<sub>3</sub>CH dimer with the same He...C distance,  $178 \text{ kJ mol}^{-1}$ .

The calculated mean He...<sup>1</sup>C bond energy, defined as one quarter of the dissociation energy He@adam = He + adam is  $-161 \text{ kJ mol}^{-1}$ . Regarding a positive bond energy as the basic criterion for a chemical bond, we concluded that the He...<sup>1</sup>C interactions were *antibonding* (destabilizing) rather than bonding. This interpretation has since been supported by Poater, Solà, and Bickelhaupt<sup>[6]</sup> and challenged, first by Bader and Fang,<sup>[7]</sup> and more recently by Krapp and Frenking.<sup>[8]</sup>

Krapp and Frenking pointed out that a negative bond energy does not always rule out the existence of a stable molecule: Thus the He<sub>2</sub><sup>2+</sup> molecule has been shown experimentally to have a mean lifetime longer than 5 μs in the gas phase and a bond length of about 75 pm.<sup>[9]</sup> Calculated potential-energy curves,  $V(R)$ , display a local minimum at  $R_e = 70 \text{ pm}$  followed by a local maximum at  $R = 217 \text{ pm}$  with energy  $140 \text{ kJ mol}^{-1}$  above the local minimum. Beyond this maximum the energy decreases monotonically with increasing internuclear distance to an asymptotic value  $840 \text{ kJ mol}^{-1}$  below the local minimum.<sup>[10,11]</sup> In spite of a large negative dissociation energy, the barrier to dissociation,  $140 \text{ kJ mol}^{-1}$ , is sufficiently high to give estimated life times of He<sub>2</sub><sup>2+</sup> molecules in the lowest vibrational and rotational state of the order of  $10^4 \text{ s}$  or about three hours.<sup>[10]</sup> This example is sufficient to show that negative bond energy does not rule out the formation of a chemical bond. Krapp and Frenking are absolutely right, our definition of a chemical bond is clearly inadequate!

Krapp and Frenking based their discussion of bonding in He@adam on the definition of a chemical bond introduced by Pauling<sup>[12]</sup> and adopted by IUPAC<sup>[13]</sup>: "There is a chemical bond between two atoms or groups of atoms in the case that the forces acting between them are such as to lead to the formation of an aggregation with sufficient stability to make it convenient for the chemist to consider it as an independent 'molecular species'".<sup>[12]</sup> Krapp and Frenking remark that this definition "does not say that there must be attractive forces

that lead to the formation of an aggregation", and since AIM analysis shows that the He atom is connected to the four tertiary carbon atoms by atomic interaction lines, and since the energy of the He atom in the complex obtained by AIM analysis is found to be lower than that of the free atom, they concluded that a description in terms of a He...<sup>1</sup>C chemical bonds seemed "reasonable". To us it seems evident that stable aggregates will only be formed if the net effect of all interatomic forces is attractive. This does not rule out the possibility that some atom-pair interactions in the aggregate are repulsive, but in such cases it is the attractive interactions that lead to the formation of an aggregation, while the repulsive interactions oppose it.

The requirement that the aggregation should have a significant life time means that there must be a sufficiently high potential barrier to dissociation. Application of the Pauling/IUPAC definition of chemical bond to the He<sub>2</sub><sup>2+</sup> species lead to the conclusion that a chemical bond is formed, because of a short range ( $R < 170 \text{ pm}$ ) attraction between the two He<sup>+</sup> ions that stabilizes the equilibrium structure relative to the transition state. A similar application of the Pauling/IUPAC definition to the He@adam complex would require us to identify the attractive forces that prevent dissociation.

**The barrier to dissociation of He@adam:** The adamantane molecule may be described as consisting of four fused six-membered rings with alternating <sup>1</sup>C and <sup>2</sup>C atoms. For the complex to dissociate, the He atom must exit through one of these rings. Optimization of the transition state under C<sub>3v</sub> symmetry showed that the He atom was at the center of gravity of the ring with three He...<sup>1</sup>C distances of 163.2 pm and three He...<sup>2</sup>C distances of 165.8 pm (see Figure 1).<sup>[1]</sup> While the equilibrium structure is characterized by four short He...C distances below 170 pm, in the transition state structure by is characterized by six such distances. The six <sup>1</sup>C-<sup>2</sup>C bond lengths in the ring have increased from 160.5 to 170.2 pm, and the energy of the transition state He@adam<sup>‡</sup> was  $172 \text{ kJ mol}^{-1}$  above that of the equilibrium structure.

We now estimate the deformation (or strain) energy of adamantane molecule in the transition state by comparing the energy of an adamantane molecule calculated with the geometry it adopts in the transition state,  $E(\text{adam}^\ddagger)$ , with the energy of calculated for its equilibrium structure  $E(\text{adam})$  [Eq. (5)]. Secondly we calculate the He...C interaction (repulsion) energy in the transition state from Equation (6).

$$\Delta E_{\text{def}}^\ddagger = E(\text{adam}^\ddagger) - E(\text{adam}) = 184 \text{ kJ mol}^{-1} \quad (5)$$

$$\Delta E_{\text{int}}^\ddagger = E(\text{He@adam}^\ddagger) - E(\text{adam}^\ddagger) - E(\text{He}) = 632 \text{ kJ mol}^{-1} \quad (6)$$

Comparison with Equations (3) and (4) show that the major part, about 74%, of the barrier to dissociation is due to an increase of the strain energy of the adamantane cage, while 26% is due to an increase of the He...C repulsion energy.

The He...C repulsion energy in the transition state is presumably determined by the diameter of the unique C<sub>6</sub> ring defined as the distance between C atoms at opposite corners Ring diameter = He...<sup>1</sup>C + He...<sup>s</sup>C = 329 pm.

What happens if the diameter of the ring is increased? To find an answer to this question we constructed a geometric model of an adamantane molecule in which the diameter of one ring had been increased to 400 pm, *adam*<sup>#</sup>.<sup>[14]</sup> The strain energy of this model, calculated from Equation (7), is 980 kJ mol<sup>-1</sup> higher than in the equilibrium structure.

$$\Delta E_{\text{def}}^{\#} = E(\text{adam}^{\#}) - E(\text{adam}) = 1044 \text{ kJ mol}^{-1} \quad (7)$$

The energy calculated for a model of the He@*adam* complex where the He atom was placed inside the *adam*<sup>#</sup> cage at the threefold symmetry axes and at a distance of 160.5 pm from the symmetry-unique (apical) <sup>1</sup>C atom was  $\Delta E_{\text{f}}^{\#}(\text{He}@\text{adam}^{\#}) = 1342 \text{ kJ mol}^{-1}$  or  $697 \text{ kJ mol}^{-1}$  above the equilibrium structure. The He...C repulsion energy for this expanded-ring model is given by Equation (8) and is  $283 \text{ kJ mol}^{-1}$  below the He...C repulsion energy of the equilibrium structure.

$$\Delta E_{\text{int}}^{\#} = E(\text{He}@\text{adam}^{\#}) - E(\text{adam}) - E(\text{He}) = 298 \text{ kJ mol}^{-1} \quad (8)$$

This means that if the adamantane frame had been more flexible, that is, if the difference between the strain energies of *adam*<sup>#</sup> and *adam*<sup>\*</sup> had been less than  $282 \text{ kJ mol}^{-1}$ , the energy of the He@*adam*<sup>#</sup> structure would have been below that of the calculated for the equilibrium structure, and the geometric deformation He@*adam* → He@*adam*<sup>#</sup> would occur spontaneously.

Calculations on He@*adam*<sup>#</sup> models in which the unique He...C distance was increased stepwise from 160 to 230 pm, showed that the energy of the complex decreased monotonically with increasing He...C distance.

In our view the results of these calculations are sufficient to show that the spontaneous dissociation of He@*adam* is prevented solely by the rigidity of the adamantane framework, that is, by the strong attractive forces between the C atoms in the cage. Dissociation through distortion to a complex of structure He@*adam*<sup>#</sup> would in fact be favored by a monotonous decrease of the He...C repulsion energy.

**AIM analysis of He@*adam* and the transient He...H<sub>3</sub>CH dimer:** AIM analysis of the charge density calculated for the transient species He...H<sub>3</sub>CH optimized under C<sub>3v</sub> symmetry

with the He...C distance fixed at 162.1 pm yields an atomic interaction line between the He and C atoms, but not between the He and H atoms. In Table 1 we compare the He...C bond critical point (BCP) parameters of He...H<sub>3</sub>CH with the He...<sup>1</sup>C BCP parameters obtained by AIM analysis of He@*adam*. As pointed out by Bader and Fang,<sup>[7]</sup> the charge densities  $\rho(r_c)$ , the density Laplacians  $\nabla^2\rho(r_c)$ , and the energy densities  $H(r_c)$  at the He...<sup>1</sup>C BCPs in He@*adam* are similar to those found for metal-carbon bonds in transition-metal carbonyls: AIM analysis of Cr(CO)<sub>6</sub>, Fe(CO)<sub>5</sub> and Ni(CO)<sub>4</sub> have yielded charge densities at the BCP's ranging from 0.10 to 0.14 au; density Laplacians ranging from 0.45 to 0.55 au, and energy densities ranging from -0.030 to -0.055 au.<sup>[16]</sup> Inspection of Table 1 will make it clear, however, that the BCP parameters of He@*adam* are much closer to those of He...H<sub>3</sub>CH than to those of the transition-metal carbonyls. Indeed, the close similarity of the BCP parameters in He@*adam* and He...H<sub>3</sub>CH strongly suggests that the nature of the He...C interactions in the two species is essentially equal.

Calculation of atomic energies or atomic charges by AIM analysis rests on the decision to describe the molecule as consisting of nonpenetrating atoms separated by sharply drawn boundary surfaces: this description is not forced on us by quantum mechanics. After the choice has been made, the theory rests on the rigid application of quantum mechanics. In Table 1 we list the AIM energies of He, C, and H atoms in He@*adam* relative to those obtained for free He atom or adamantane molecule. It is seen that the AIM energy of the He atom in the complex is lower than that of the free atom. Calculation of atomic energies in transient species like He...H<sub>3</sub>CH is possible, but not routine.<sup>[17]</sup> Calculation of the atomic energies of He...H<sub>3</sub>CH for comparison He@*adam* would, however, be of great interest.

Bader and Fang<sup>[7]</sup> have shown that the Ehrenfest forces acting across the interatomic surfaces between the He and <sup>1</sup>C atoms in He@*adam* are attractive. In view of the similarity between the BCP parameters of He@*adam* and He...H<sub>3</sub>CH, it would be of considerable interest to know whether the same is true for the Ehrenfest forces acting between the He and C atoms in the transient methane species.

## Addendum

**Note added in proof:** In this communication we have searched for the origin of the high energy of formation of the inclusion complex He@*adam* by partitioning the energy

Table 1. He...C bond critical point parameters for He@*adam* and He...H<sub>3</sub>CH with the He...C distance fixed at 162.1 pm: distances to attractors, charge densities  $\rho(r_c)$ , density Laplacians  $\nabla^2\rho(r_c)$ , Hessian eigenvalues  $\lambda_1$ ,  $\lambda_2$ , and  $\lambda_3$ , and energy densities  $H(r_c)$ . AIM atomic energies relative to free He atoms or adamantane molecules.<sup>[a]</sup>

	Distances to attractors [pm]	$\rho(r_c)$ [au]	$\nabla^2\rho(r_c)$ [au]	$\lambda_1 = \lambda_2$ [au]	$\lambda_3$ [au]	$H(r_c)$ <sup>[b]</sup> [au]	$\Delta E(\text{He})$ [kJ mol <sup>-1</sup> ]	$\Delta E(\text{C})$ [kJ mol <sup>-1</sup> ]	$\Delta E(\text{H})$ [kJ mol <sup>-1</sup> ]
He@ <i>adam</i>	72.1–90.0	0.078	0.362	-0.076	0.513	-0.018	-1263	218 <sup>[c]</sup> ; 137 <sup>[d]</sup>	16 <sup>[e]</sup> ; 13 <sup>[f]</sup>
He...CH <sub>4</sub>	71.5–90.6	0.071	0.346	-0.083	0.512	-0.013			

[a] All parameters calculated at the B3LYP/6-311++G(2p,2d) level<sup>[1]</sup> unless otherwise noted. [b] Calculated at the RI-BP86/def2-TZVPP level.<sup>[15]</sup> [c] Four tertiary C atoms. [d] Six secondary C atoms. [e] Hydrogen atoms bonded to tertiary C atoms. [f] Hydrogen atoms bonded to secondary C atoms.

of formation into deformation and interaction energies. Our analysis leads to the conclusion that the high energy of formation is due to strongly destabilizing interactions between the He atom and the four tertiary C atoms. In the following communication Hoffgarten and Frenking analyze the energy of formation by partitioning the energies of the free adamantane molecule and of the complex into atomic energies based on AIM analysis of the charge densities. Their investigation leads to the conclusion that the He...C interactions in the complex are stabilizing. This stabilization is, however, more than canceled by a concomitant weakening of the C–C bonds. The reader is thus faced with two alternative interpretations, each valid within each own conceptual framework, and is free to choose the one that he finds most convenient.

In the final paragraph of their communication Hoffgarten and Frenking write: “We think that the arguments against the presence of He–C chemical bonds in He@adam given by Strenalyuk and Haaland are valid within the realm of classical bonding models. However, we also think that the AIM analysis provides compelling evidence for the opposite view. In our view, the physical view of chemical bonding advocated by Bader and Fang is more sound and goes deeper when it comes to fundamental laws of physics than the chemical view of Strenalyuk and Haaland which is based on the pragmatic approach that is typical for chemistry.” We do not share these views;

i) Our calculations of deformation and interaction energies are based on quantum mechanics and the Born–Oppenheimer approximation. AIM atomic energies are based on charge densities calculated on the same basis plus the somewhat arbitrary decision to regard the molecules as composed of non-penetrating atoms. Our interpretation may be more in line with classical bonding models, but we cannot see that it is less firmly based on quantum mechanics or less compelling than an interpretation in terms the atomic energies or Ehrenfest forces obtained by AIM analysis.

ii) The AIM energy of the individual atoms in a general polyatomic molecule cannot be determined experimentally. For a discussion of this point, see reference [18]. The deformation energy of the adamantane molecule in the complex may—at least in principle—be determined by studying the symmetric deformation frequencies. Since the interaction energy is defined as the difference between formation and deformation energies,  $\Delta E_{\text{def}}$  and  $\Delta E_{\text{int}}$  are both observable. It is not obvious to us that an interpretation in terms of non-observable quantities should be regarded as “going deeper” than an interpretation in terms of observable ones.

We also note that our simple interpretation leads immediately to hypotheses that may be tested. Our analysis thus suggests that the energy of formation of a complex of a rare gas atom in a hydrocarbon cage will increase with the radius of the rare gas atom and decrease with increasing radius of the cage. As far as we know this hypotheses is consistent with the results of all computational studies of such complexes up to the present.<sup>[19]</sup>

Our final point concerns terminology. We believe that we have demonstrated that the He...C interactions in He@adam do not correspond to “chemical bonds” according to the Pauling/IUPAC definition. This classical, well-established definition is based on an observable property, namely, the lifetime of the species. To describe the He...C interactions in He@adam as “genuine bonds” or as “chemical bonds” is in our view tantamount to adopting a new, and nonequivalent definition of the concept based on nonobservable parameters.

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**Keywords:** chemical bonds • dissociation reactions • helium • inclusion compounds • reaction barriers

- [1] A. Haaland, D. J. Shorokhov, N. V. Tverdova, *Chem. Eur. J.* **2004**, *10*, 4416.
- [2] I. Hargittai, K. Hedberg, *J. Chem. Soc. Chem. Commun.* **1971**, 1499; I. Hargittai, K. Hedberg in *Molecular Structure and Vibrations* (Ed.: S. J. Cyvin), Elsevier, **1972**, p. 340.
- [3] T. A. Halgren, *J. Am. Chem. Soc.* **1992**, *114*, 7827.
- [4] B. P. Reid, M. J. O’Loughlin, R. K. Sparks, *J. Chem. Phys.* **1985**, *83*, 5656.
- [5] R. F. W. Bader, *Atoms in Molecules: A Quantum Theory*, Oxford University Press, Oxford, **1990**.
- [6] J. Poater, M. Solà, F. M. Bickelhaupt, *Chem. Eur. J.* **2006**, *12*, 2889; J. Poater, M. Solà, F. M. Bickelhaupt, *Chem. Eur. J.* **2006**, *12*, 2902.
- [7] R. F. W. Bader, D.-C. Fang, *J. Chem. Theory Comput.* **2005**, *1*, 403.
- [8] A. Krapp, G. Frenking, *Chem. Eur. J.* **2007**, *13*, 8256.
- [9] A. Belkacem, E. P. Kanter, R. E. Mitchell, Z. Wager, B. J. Zabransky, *Phys. Rev. Lett.* **1989**, *63*, 2555.
- [10] J. Ackermann, H. Hogreve, *J. Phys. B* **1992**, *25*, 4069.
- [11] M. Kolbuszewski, J.-P. Gu, *J. Chem. Phys.* **1995**, *103*, 7649.
- [12] L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, New York, **1960**, p. 6.
- [13] IUPAC Compendium of Chemical Terminology, 2nd ed., **1997**.
- [14] The model was constructed by leaving the *z* coordinates of the six C atoms in the ring unchanged while the *x* and *y* coordinates were multiplied by a scale factor chosen to yield distances He...C and He...C distances equal to 197.9 and 202.6 pm, respectively. The coordinates of the four remaining C atoms and all H atoms were optimized with a He atom retained at the center of symmetry-unique ring.
- [15] G. Frenking, private communication.
- [16] F. Cortés-Guzmán, R. F. W. Bader, *Coord. Chem. Rev.* **2005**, *249*, 633.
- [17] R. F. W. Bader, *J. Phys. Chem. A* **2007**, *111*, 7966.
- [18] R. G. Parr, P. W. Ayers, R. F. Nalewajski, *J. Phys. Chem. A* **2005**, *109*, 3957.
- [19] See, for instance: D. Moran, H. L. Woodcock, Z. Zhen, H. F. Schaefer III, P. van R. Schleyer, *J. Am. Chem. Soc.* **2003**, *125*, 11442 and R. B. Darzynkiewicz, G. E. Scuseria, *J. Phys. Chem. A* **1997**, *101*, 7141.

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