DOI: 10.1002/chem.201000789

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Antibond Breaking—The Formation and Decomposition of He@Adamantane: Descriptions, Explanations, and Meaning of Concepts

Shu-Guang Wang,[a, b] Yi-Xiang Qiu,[a] and W. H. Eugen Schwarz*[a, b, c]

Dedicated to Professor Klaus Ruedenberg on the occasion of his 90th birthday

Abstract: The reaction path from the inclusion complex He@adamantane to its two separated fragments over the transition barrier is investigated by using quantum chemistry. The changes of structure and wavefunction are intuitively anticipated, accurately computed, and qualitatively rationalized. With the help of the traditional concepts of chemical bonding and nonbonding interactions, and with numerical results from a chemically oriented energy-partitioning approach, we can rationalize the details of the chemical process, and qualitatively predict and interpret the two chosen alternative descriptions: the energy-partitioning approach and the topological electron-density analysis. The meaning of bonding within these two approaches, and unsolved aspects of the latter tool are clarified.

Keywords: bond theory • cage compounds • electron-density analysis • quantum chemistry • reaction barriers

Introduction

In chemistry, the mission of theory is threefold: computational prediction, numerical description, and qualitative explanation.

1) Ab initio or semiempirical *computations* yield predictions (or reproductions) of static and dynamic properties of molecules and materials. The metastable molecular title compound has already been investigated several times.[1–7] Here, we will apply a quantum computational approach (nonrelativistic density functional theory (DFT) at the lowest-order Born–Oppenheimer (BO) approximation, and also some post-Hartree–Fock MP2 calculations) that reproduces the known (experimentally derived and computed) data reasonably well.

2) Detailed *descriptions* of stationary and time-dependent states can be achieved with the help of their wavefunctions and various observables and, at a minimal level, of their charge-density distributions. Among the many available tools, we will here apply some common analyses of geometric structures and energies, and also the so-called topological analysis of electron densities (quantum theory of atoms in molecules, QTAiM), which leads to 'revolutionary' pictures.[8,9]

3) Causal–physical *explanations* should rationalize why the chemical system behaves as observed or computed, and as described by the various description tools. According to the IUPAC definition[10] (which, however, has not received full support),[8e,11] there exist interatomic bonds in the case of atomic aggregates of sufficient stability (such as for He@adamantane). Several aspects are relevant here.

Why and how does the Schrödinger equation generate a sufficiently stable situation? To understand chemical bonding, we must first specify the meaning of stability, that is, we must compare the stable or metastable system with a judiciously chosen reference of higher energy. Then, we may try to rationalize the eigen-energy change between the Hamiltonians of the stable system and the less stable reference. Third, nature achieves the equilibrium states, for example, of the components and of the compound aggregate, each time by a delicate balance of several physical tendencies,

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[a] Prof. Dr. S.-G. Wang, Dr. Y.-X. Qiu, Prof. Dr. W. H. E. Schwarz
WG of Theoretical Chemistry, Department of Chemistry
Shanghai Jiao Tong University, 200240 Shanghai (China)
Fax: (+86) 21 5474 1297
E-mail: schwarz@chemie.uni-siegen.de

[b] Prof. Dr. S.-G. Wang, Prof. Dr. W. H. E. Schwarz
AG Theoretische Chemie, FB 8
Universität Siegen, 57068 Siegen (Germany)

[c] Prof. Dr. W. H. E. Schwarz
Theoretical and Computational Chemistry Lab
Chemistry Department, Tsinghua University Beijing
100084 Beijing (China)

Supporting information (containing additional numerical details) for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201000789.

contributing large values of different signs to the total energy. Thereby, the more complex hierarchies of material structures emerge.

The physical mechanism may be understood through Ruedenberg's 'variational reasoning'.[12,13] Often paradoxical situations show up. For instance, covalent bonding originates in a reduction of the kinetic-energy density, but exhibits an increase of the kinetic-energy value. Or a spin triplet state has a negative sign in the exchange-Coulomb expression, but often has a higher two-electron Coulomb repulsion energy value than the respective singlet.

Our philosophy of explanation shall aim at such a partitioning of the total energy change so that the explanatory components are not huge and of opposite signs. That is, the total effect shall be described by a very few noncanceling terms. Thereby the sign of the effect will become obvious and intuitively understandable. We will apply the energy-partitioning scheme in each case in such a manner that is adapted to the case at hand.[12] Physical phenomena can often be described in close detail, but as marginal results of a well-established competition between various strong and opposite tendencies (such as bonding in Morokuma's, Weinhold's, or Bader's approaches).[8,9,14,15] Here, we shall explain them through single dominant constructs of terms, and smaller remainders. The aim is achieved by molecule-adapted sums of terms from the energy decomposition analysis (EDA, sometimes also called the energy partitioning approach, EPA) of Morokuma, as modified by Ziegler and Baerends (MZB).[15,16] We will apply the procedure along the path of decay (or formation) of the He@adamantane complex over the transition state (TS) to the components (fragments) He and adamantane.

It is a matter of taste or philosophical standpoint whether one is only interested in one or more types of descriptions of objective reality (communicating more or less details) or also in more or less subjective rationalizations and explanations (aiming at an intuitive understanding of the facts). We follow the motto that models of chemical bonding need not only be rooted in quantum mechanics, but should also provide intuitive insight, possess predictive power, and thereby be chemically productive.[17] The title compound is a good example, in which qualitative chemical concepts are corroborated and quantified by ab initio based explanations, and where even the chemically counterintuitive QTAiM descriptions can be predicted qualitatively.

Energy Partitioning

The total energy of a molecule (as well as the kinetic and potential components) is a physical observable. Its dependence on the molecular structure is an important indicator of the type of interatomic interactions. Chemists like to understand this observable in terms of empirical diatomic bond-energy increments (and, in specific cases, of additional polycentric mesomeric and neighboring-group effects). Two completely different types of energy-partitioning schemes are available, namely, the aforementioned atomic-plus-bond schemes, and also purely one-center atomic schemes (besides intermediate ones).[8,9,15,16,18]

Different viewpoints sometimes lead to seemingly divergent *descriptions* of the actual bonding situation, which may even be obscured by different meanings attached to the same words. Martín-Pendás et al.[18] have stressed that, depending on the collection scheme of differential energy terms, we may obtain different views. For instance, in the approach of interacting quantum atoms (IQA), which is the energy-partitioning scheme within the topological QTAiM approach,[9] the changes of the electronic kinetic energy are counted as one-center atomic deformation effects upon interatomic interaction, whereas they are counted as multicenter Pauli repulsion or covalent attraction terms causing the interatomic interaction in the EDA approach. As long as the energy-partitioning scheme yields unique contributions and the correct sum for the bond energy, it is acceptable in principle. Partitioning schemes supporting *physical explanations*, possibly adapted to the case under investigation,[12] should produce, as argued above, only a (very few) dominant or decisive energy contribution(s), at best of the same sign. Further, it seems to us as an advantage, if the empirically derived, practically successful, traditional concepts (the reality-adapted noumena of chemists)[19,20] can be somehow related to the various quantum-theoretical constructs.

According to the chemical concepts, molecular structure and reactivity are governed by various kinds of primary bonds, secondary attractions, and nonbonding repulsions. Primary bonding means diatomic energy-lowering increments (ΔE) of more than approximately 100 $\mathrm{kJ\,mol^{-1}}$ (with respect to commonly chosen references), at equilibrium bond lengths R_e (defined by $\partial\Delta E/\partial R\,|_{R_e}=0$) corresponding to sums of common atomic bond radii, and with bond-stretching force constants ($k=\partial^2\Delta E/\partial R^2\,|_{R_e}$) of the order of $\mathrm{N\,cm^{-1}}$. Secondary bonding[21] may be as small as a few $\mathrm{kJ\,mol^{-1}}$, at distances shorter than the sums of common van der Waals radii, and it may be caused by dispersion, by multipolar direct and polarizing interactions, and/or by weak orbital-interference effects. Nonbonding repulsions play a role in collision processes, in condensed phases, and in overcrowded molecules, which are pressed together by stronger attraction forces between other groups of atoms than the nonbonded ones. A specific class of compounds are the endohedral inclusion complexes (IC) and clathrates, which are kept together within the components, though without any traditional bonds between their components. They are solely due, in the eyes of chemists proper, to the three-dimensional arrangement of atoms and bonds in the whole network. The trapping effect of the IC that outstrips the antibonding repulsions between the components has recently been discussed under the rubric of 'confinement'.[5]

In the case of the title compound, either strong destabilizing (MZB-EDA) or strong stabilizing (QTAiM-IQA) interactions were postulated between the components of the IC (noble gas atom He and saturated closed-shell adamantane cage).[2–7] Paradoxical bond descriptions are also well known for several other complexes.[22] In the case at hand, the IC is unstable with respect to its fragments, at a rather high-energetic local minimum of the potential-energy hypersurface (PES); it is stable only with respect to the TS. Therefore, our reference states should comprise both the energetically lower decay products, and the higher-energetic saddle point at the TS.

The MZB-EDA scheme: The traditional bond concepts can be pictured well with the help of MZB-EDA.[15,16] The interaction energy, ΔE, of an aggregate A–B with respect to properly chosen fragments A,B is represented as a sum of four contributions (which may each be decomposed further, for example, in kinetic and potential terms, except the electrostatic energy, E_{elstat}) as shown in Equation (1):

$$\Delta E = E_{\mathrm{def}} + E_{\mathrm{elstat}} + E_{\mathrm{Pauli}} + E_{\mathrm{orb}} \tag{1}$$

The deformation energy (E_{def}) is the energy difference of the separated fragments A,B (represented by $\Psi^{\mathrm{o}}_{\mathrm{A}}$ and $\Psi^{\mathrm{o}}_{\mathrm{B}}$, perhaps with appropriately occupied open shells) between their geometric–electronic minima and the geometries as in the bonded aggregate. E_{def} is antibonding (positive), though often comparatively small. The electrostatic energy (E_{elstat}) of the overlaid fragments is usually attractive (negative), in particular for strongly overlapping shells. The last two terms refer to the intermediate construct of a nonstationary physical state of the overlaid fragments as shown in Equation (2):

$$\Psi^{\mathrm{o}}_{\mathrm{overlay}} = N \cdot \mathrm{A}(\Psi^{\mathrm{o}}_{\mathrm{A}} \cdot \Psi^{\mathrm{o}}_{\mathrm{B}}) \tag{2}$$

$\Psi^{\mathrm{o}}_{\mathrm{overlay}}$ is the lowest-order perturbation theoretic state function of the aggregate of minimally modified fragments in the quantum framework. An alternative to the quantum mechanical overlay of wavefunctions, $\Psi^{\mathrm{o}}_{\mathrm{A}}\cdot\Psi^{\mathrm{o}}_{\mathrm{B}}$, is the classical overlay of densities, $\rho'^{\mathrm{o}}_{\mathrm{overlay}}=\rho^{\mathrm{o}}_{\mathrm{A}}+\rho^{\mathrm{o}}_{\mathrm{B}}$, and the search for that intermediate compound wavefunction $\Psi'^{\mathrm{o}}_{\mathrm{overlay}}$ that minimizes the energy for $\rho'^{\mathrm{o}}_{\mathrm{overlay}}$.[23] The antisymmetrization operator A accounts for the Pauli principle, and N is the normalization factor. The respective energy increase is the Pauli repulsion (E_{Pauli}) of the overlapping core and valence shells of the fragments with electrons of the same spin. The dominant contribution is of kinetic origin: the required orbital orthogonalization creates additional nodes. The sum of the two or three terms [Eq. (3)] is called the steric energy (E_{ster}) of the fragments in the aggregate.

$$\Delta E_{\mathrm{ster}} = (E_{\mathrm{def}}+)E_{\mathrm{elstat}} + E_{\mathrm{Pauli}} \tag{3}$$

Finally, E_{orb} is the attractive-energy improvement by optimal electron redistribution in the relaxed spin orbitals of the compound system. It comprises interference, polarization, charge transfer, and correlation contributions. (In particular the interference term is sensitive to the choice of the details of open-shell fragment states.)

The antibonding Pauli interaction, which forms an important ingredient of EDA, and of traditional chemical argumentation, has from time to time been sternly rejected, for example, in a paper entitled “Pauli Repulsions Exist Only in the Eye of the Beholder”.[8b,d] It has been argued that there is only one important basic force at the atomic level of chemistry, namely, the Coulomb force, and that is certainly true. The Coulomb force yields the Hellmann–Feynman force (HFF) of the electrons and other nuclei on the chosen nucleus, and also the Ehrenfest force on a chosen piece of electronic charge distribution.[24] Three remarks are in order here:

1) The electron-density distribution must be known at a quite high level of accuracy to get at least the correct sign for the HFF. Although approximate molecular energies can be obtained from approximate density distributions[25] or wavefunctions, this is not the case for the HFF.[26] For instance, the approximate HFFs are significantly repulsive for the so-called promolecules (i.e., the overlays of undeformed, spherical atoms or components at molecular equilibrium geometry).[27] Particularly impressive is the case of a cation and an anion.[28] [Silberbach[28] has discussed the extreme case of two interacting, but unperturbed spherical ions A^- and K^+ at large distance R, at which the approximate HFF of A^- on K^+ and of K^+ on A^- are $+Z_{\mathrm{A}}/R^2$ and $-Z_{\mathrm{K}}/R^2$, and the correct value for both cases is $-1/R^2$.] Since the HFF is “extraordinarily sensitive”, one must correct it in all practical cases, even for good-quality wavefunctions, by the Pulay force.[29] The latter can be computed routinely from an approximate wavefunction, but has no simple visualization or clear appeal in terms of the density.

2) By knowing the correct nuclear forces (e.g., zero at known equilibrium nuclear geometry), one can conversely improve the equilibrium electron-density distribution in the vicinity of the nuclei to reproduce the known (i.e., vanishing) HFF.[30] It is the inner tails of the valence orbitals near the nuclei that give the main contribution to the electrostatic forces on the nuclei, and less so the so-called bond densities between the nuclei.[26] The respective incorrect prejudice is very common in textbooks, and sometimes occurs even in the recent journal literature,[31] having been initiated by early papers by Slater and Feynman on the virial and force theorems.[32]

3) The discussion of complex dynamical systems (e.g., molecules) can be simplified by introducing pseudoforces between the fragments, which account for the effects of the Coulomb forces and of the nontransparent kinematic and antisymmetric constraints of the elementary particles. An inertial observer in 3D space introduces only the gravitational and Coulombic central potentials into the classical or quantum Hamiltonians. However, instead of rotation in space with angular momentum L at distance r from the center, one may change to a motion in a single dimension r with an additional centrifugal potential $V_{\mathrm{rot}}=L^2/2\mathrm{m}r^2$ (m = electronic mass) and centrifugal force $F=L^2/\mathrm{m}r^3$. Another example is the van der Waals pseudoforce between non-overlapping neutral atoms and molecules as the result of the Coulombic stray fields due to electron correlation. The Pauli repulsion is also a dynamical pseudoforce. The exchange-antisymme-

try requirement for Fermionic wavefunctions according to the Pauli principle may be replaced by an 'occupation exclusion pseudopotential'.[33] Fermi–Dirac statistics for many-electron systems, that is, the occupation of higher momentum cells in phase space for higher particle densities at a given position, or the occupation of orthogonalized orbitals with additional nodes, both mean a higher kinetic energy density. The energy increase is slightly modified for open valence shells, since the Coulomb repulsions between the electrons are a little larger ($J+K$) or smaller ($J-K$) than at the average value (J), respectively, for opposite or similar spin directions. A more explicit nomenclature—for example, $J=$ 'direct Coulomb integral' instead of 'Coulomb integral', $K=$ 'exchange Coulomb integral' instead of 'exchange integral'—would support the understanding in the chemical community. The statement that "exchange always reduces the electron–electron repulsion"[8d] does not hold for the singlet, even if one omits the dominant (!) exchange-antisymmetry effect. The kinetic-energy contribution T is often overlooked in bond-energy discussions,[31] although it is comparable in magnitude to the total energy, according to the virial theorem $T=-E-R\cdot\nabla_R E$ (R = internuclear distance).[32a,34]

Expectations of He + adamantane: Adamantane is a saturated cage of four fused, puckered cyclohexane rings, $(^{t}CH)_4$-$(^{s}CH_2)_6=C_{10}H_{16}$. In the case of the IC He@adamantane (Figure 1 left), the formation energy from $He+C_{10}H_{16}$ is repulsive by about +640 kJ mol^{-1}.[2,5] The MZB energy partitioning yields a huge Pauli repulsion of about +1080 kJ mol^{-1} and a small adamantane deformation energy of about +60 kJ mol^{-1}. This energetic destabilization is somewhat reduced by electrostatic overlap attraction (about −300 kJ mol^{-1}) and orbital relaxation (about −200 kJ mol^{-1}) so that a large antibonding energy of +640 kJ mol^{-1} survives. The metastability of the IC is due to a decay barrier of about +170 kJ mol^{-1}. The alternative partitioning developed within QTAiM in contrast yields a significant He–adamantane closed-shell 'QTAiM stabilization' that is largely overcompensated by a drastic destabilizing energy increase of the adamantane fragment of the IC.[3,4]

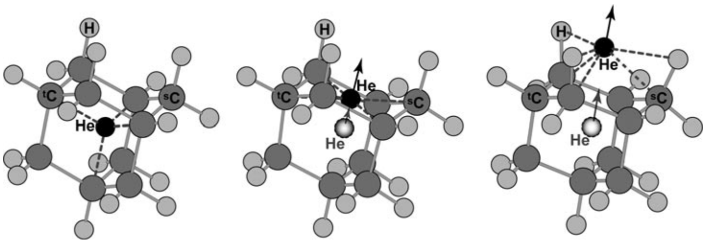

Figure 1. He@adamantane decay along a C_{3v} symmetry axis. Left: Equilibrium structure (of T_d symmetry) with four He···^{t}C contacts. Middle: TS of the He atom leaving the cage upwards through a weakly puckered C_6 ring, with three He···^{s}C contacts and three He···^{t}C contacts. Right: State of largest ^{s}CH–^{s}CH angle deformation of the adamantane, with three He···^{s}C contacts and three He···H(^{s}C) contacts.

What do we now expect, when a He atom approaches the cage from the outside (see Figure 1)? First, we speculate in terms of the conventional chemical concepts. The entrance gate consists of a cyclohexane ring, with three upwards-pointing, nearly parallel ^{s}C–H groups. The H···H distances of 256 pm in free adamantane will widen up because of closed-shell repulsions at the three He···H(^{s}C) contacts. The ^{s}C–H/^{s}C–H angles will open up, creating some angle-deformation energy. Then, the overlap between He and the saturated carbon atoms of the C_6 entrance ring will increase. Significant He–C_6 Pauli repulsions causing adamantane deformation will create an energy maximum when He is near the C_6 center. At this TS, the C_6 ring will be stretched and less puckered. When the He atom reaches the center hole of the cage, we expect some energy decrease towards the metastable equilibrium state of the IC. There will be six He···C contacts at the TS, and four slightly shorter ones in the IC.

In the background of this physical understanding, and of the experience with QTAiM,[3,4] we may now predict the QTAiM description of the He@adamantane formation process. At first, the three He···H contacts will give rise to three atomic interaction lines (AILs) of maximal electron density, the so-called 'bond paths',[51] corresponding to the above-mentioned MZB-Pauli repulsions. A QTAiM stabilization between He and the saturated hydrogen atoms is expected, which pushes the hydrogen atoms away due to overcompensation by the deformation energy increase of the adamantane fragment. When He approaches the C_6 entrance gate, the six He···C contacts will give rise to six chemically MZB-antibonding, QTAiM-stabilizing AILs. Finally, the three He···^{s}C AILs will break and a fourth Pauli-repelling He···^{t}C AIL will form to approach the equilibrium situation of He@adamantane with four equivalent He···^{t}C AILs.

The individual numerical values and parameters must now be estimated computationally. We will determine the structures, energies, and electron densities. We will then present a chemically oriented EDA-MZB explanation. We will also present a formally oriented topological QTAiM density description and explicate the meaning of the two different approaches.

Computational Methods

Calculations were performed at the Kohn–Sham density functional level with the Vosko–Becke–Perdew functional (i.e., BP86, but with Vosko–Wilk–Nusair (VWN) as the local density approximation (LDA), method I) and with B3LYP (method II).[35] In addition, MP2 calculations were performed (method III). In method I, valence triple-zeta double-polarization Slater-type basis sets were applied, as given in the program package ADF2007.[36] Gaussian-type sets 6-311++G(2d,2p)/aug-cc-pVQZ (for C, H/He) as available in GAUSSIAN03 were used with methods II and III.[37] The basis-set superposition errors were corrected by the common counterpoise recipe.[52]

The geometric structures were optimized (including the counterpoise correction) along the reaction pathway from the free fragments (He, adamantane) through the TS to the metastable IC He@adamantane. The energies were analyzed with the MZB-EDA energy-partitioning approach (method I).[15,16] The QTAiM AILs were determined with AIM2000 (method II).[38] The reaction coordinate is R^*, the distance of He from the center of gravity of the (deformed) adamantane. $R^* = 0$ for the equilibrium IC, and $R^* \rightarrow \infty$ for the separated components.

Results

Structures from DFT (method I): When He approaches the cage along a C_3 axis, the angles between the three ^{s}C–H bonds of the entrance region are at first widened up from 2° (the value for free adamantane) to 17°, when the He is just below the H_3 midpoint (Figure 1 right, Figure 2 right, Figure 3 top).

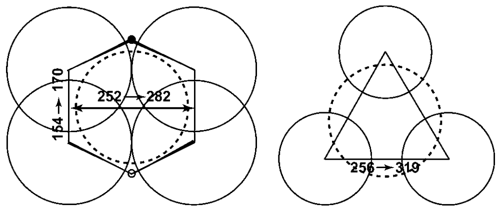

Figure 2. Left: C_6 entrance ring (full van der Waals circles of the C atoms) with the He atom in the center (dashed circle). Right: H_3 entrance group (full circles: H atoms) with He in the center (dashed circle). Numbers: C–C and H–H atom and CC–CC bond lengths, in pm; before the arrows (→): in free adamantane; after →: when He sits in the center of C_6 (left) or H_3 (right).

When He moves in further, the C_6 entry ring comes under pressure and widens and flattens (Figure 1 middle, Figure 3 middle). When He has reached the center of the C_6 entry ring at $R^* = 0.75$ Å, the three pairs of parallel C–C bonds adjacent to He are expanded by approximately 16 pm (C–C is 154.0 pm in free adamantane, 170.1 pm at the TS, and 160.4 pm in the IC, in good agreement with the literature).[2–7] The distances of the parallel pairs of C–C bonds with He in the middle have increased by approximately 30 pm (CC···CC is 252 pm in adamantane, 282 pm at the TS (Figure 2 left) and 263 pm in the IC). The CCC angles in free adamantane are all within 0.25° of the tetrahedral value of 109.5°. The C_6 entrance ring at the TS has larger angles of ^{s}C-^{t}C-^{s}C = 113.1° and ^{t}C-^{s}C-C^{t} = 110.2°. The six He–C contacts at the TS are 163.2 and 165.7 pm, slightly longer than in the IC He@adamantane (162.0 pm).

When He moves from the center of the adamantane cage to the C_6 entrance–exit ring, the C–C distances increase continuously, whereas the C–H directions at first only change very little and then more when He comes to the TS. This is indicated by the left shoulder in Figure 3 (top). Since in the IC, the He presses outwards mainly against the four ^{t}C atoms, the ^{s}C-^{t}C-^{s}C angles become smaller (108.6°) and the ^{t}C-^{s}C-^{t}C angles become larger (111.1°) than in the free adamantane. The structures from methods II and III are very similar (i.e., distances within 1 pm).

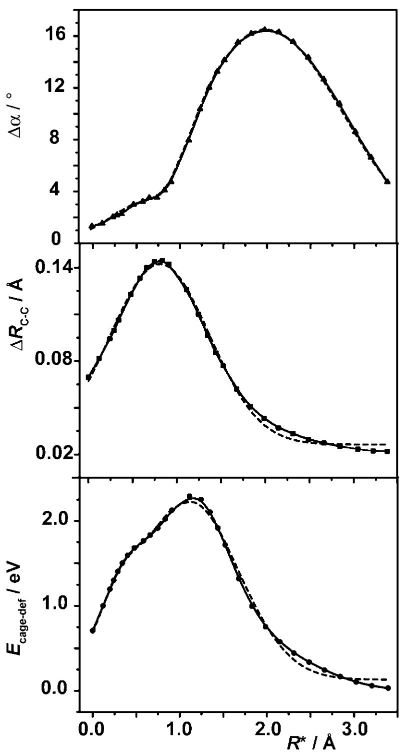

Figure 3. The He atom in the center of adamantane ($R^* = 0$) leaves the cage. R^* is the He shift in Å. The dashed lines are fits by one or two Gaussians. Top: Angle between two ^{s}C–H groups, $\Delta\alpha$ in degrees (main maximum at $R^* = 2$ Å, 0.16 Å below the H_3 midpoint, see Figure 1 right and Figure 2 right; shoulder for He at the TS). Middle: Expansion of the C–C bonds of the C_6 gate, ΔR_{C-C} in Å (maximum at $R^* = 0.81$ Å, the midpoint of the C_6 exit ring, see Figure 1 middle and Figure 2 left). Bottom: Deformation energy of adamantane, $E_{cage-def}$ in eV (maxima at $R^* = 0.3$ and 1.1 Å).

Energies from DFT (methods I, II) and MP2 (method III): Along the whole reaction path of the entrance of He into the adamantane cage, the total energy changes (**Δ***E* in Figure 4) are nearly two thirds of the Pauli repulsion energies. About one third of E_{Pauli} is approximately compensated by the electrostatic overlap attractions, that is, the so-called steric repulsion energy $E_{Pauli} + E_{elstat}$ from the lowest order of

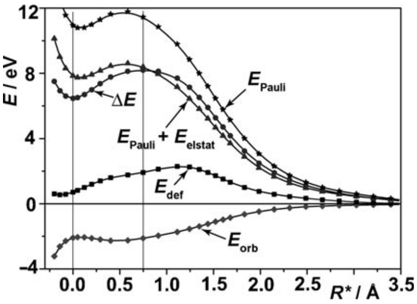

Figure 4. Energy variation (E in eV) when He leaves the center of adamantane ($R^* = 0$), He shift from adamantane center R^* in Å. ★ Pauli repulsion, E_{Pauli}; ▲ steric repulsion, $E_{Pauli} + E_{elstat}$; ● total energy, ΔE (remarkably similar to $^{2}/_{3}E_{Pauli}$); ■ cage deformation energy, E_{def}; ◆ orbital relaxation energy, E_{orb} (similar to $^{2}/_{3}E_{elstat}$).

the quantum mechanical perturbation approximation is of a similar order of magnitude as the total interaction energy. The decay energy ΔE of the stationary IC at $R^*=0$ (DFT I: 6.46 eV = 623 kJ mol^{-1}; DFT II: 6.64 eV = 640 kJ mol^{-1}; MP2: 6.17 eV = 595 kJ mol^{-1}) can be compared with the interaction energies of He···CH_4 at the respective distances.[2b,5] One can then estimate that approximately 20% (≈130 kJ mol^{-1}) of ΔE is connected with each of the four He···^{t}C AILs (distance = 162.2 pm), whereas each of the six longer He···^{s}C interactions (distance = 184.6 pm) without AILs (see below) contributes only approximately 3% (≈20 kJ mol^{-1}) of the repulsion energy.

The barrier (at $R^*=0.75$ Å) against immediate decay of the high-energy IC is 167 kJ mol^{-1} (DFT I), 173 kJ mol^{-1} (DFT II), or 191 kJ mol^{-1} (MP2, method III). (The formation barrier from the fragments is then 790, 813, or 786 kJ mol^{-1}, respectively.) E_{elstat}, E_{orb}, and E_{Pauli} vary somewhat along the reaction path from the IC to the TS, up and down, so that their summed contributions to the barrier remain small. The main contribution (120 kJ mol^{-1}, ≈70%) comes from the increased cage deformation at the TS, as already noted by Strenalyuk and Haaland.[2b] To the lowest order, the cage deformation energy should vary as approximately $k/2\Delta R^2$, which is small for small deformations of ΔR (from free adamantane to adamantane of the IC), but larger for the next amount of deformation (from the IC to the TS).

Topology of the electron densities (DFT, method II): The electron-density bridges (AILs) at several different positions R^* of He are displayed in Figure 5. We have determined the AILs both for the equilibrium structures (IC, TS, large He–adamantane distances) and for the intermediate structures, for which additional Hellmann–Feynman forces act on the nuclei.[51] The electron density and Laplacian values at the density saddle points (BCP) are displayed in Table 1.

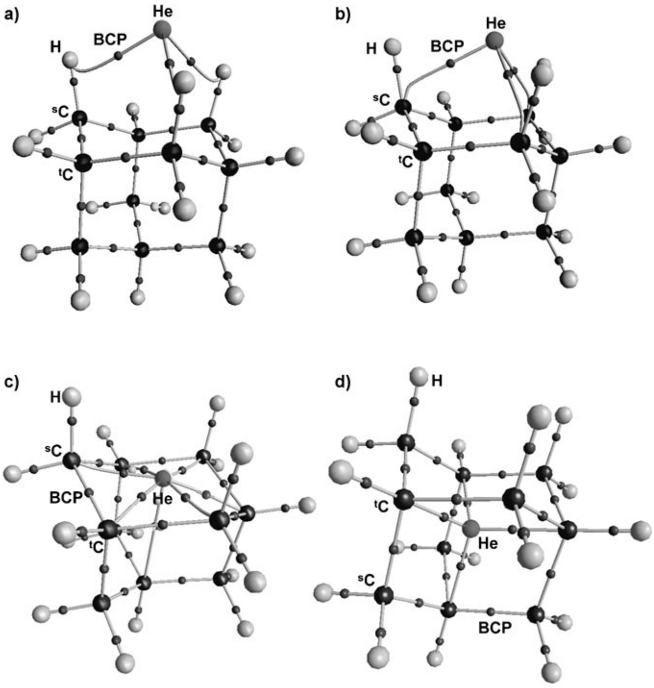

Figure 5. QTAiM interatomic density bridges (AILs) with bond critical points (BCPs). a) He is approaching three H–^{s}C groups at $R^*=2.7$ Å. b) At $R^*=2.3$ Å, the three He···H AILs have just flipped to three He···^{s}C AILs. c) At $R^*=0.8$ Å, three additional He···^{t}C AILs to the C_6 ring, and one long He···^{t}C AIL to the bottom have formed. d) At $R^*=0$, the three He···^{s}C AILs have disappeared, four equivalent He···^{t}C AILs remain in the IC at equilibrium.

Table 1. Electron density (ρ in e Å^{-3}), density Laplacian ($\Delta\rho$ in au), local energy density (H in au), local electronic kinetic energy (G/ρ in au), and bond degree ratio ($-V/G$) at the density saddle points (BCP).[a]

Position of He	He–^{t}C		He–^{s}C	He–H
outside the cage (R^*=2.66 Å)[b]	none		none	3×ρ: 0.141 $\Delta\rho$: +0.098 small values of H, G/ρ, and V/G
at the center of the H_3 triangle (R^*=2 Å)[c]	none		3×ρ: 0.275 $\Delta\rho$: +0.212 H: −0.003 G/ρ: 1.24 $-V/G$: 0.95	none
at the center of the C_6 ring (R^*=0.75 Å)[d]	3×ρ: 0.532 $\Delta\rho$: +0.376 H: −0.011 G/ρ: 1.33 $-V/G$: 1.10	1×ρ: 0.135 $\Delta\rho$: +0.118 small values of H, G/ρ, and V/G	3×ρ: 0.519 $\Delta\rho$: +0.368 H: −0.001 G/ρ: 1.32 $-V/G$: 1.09	none
in the center of the cage (R^*=0)[e]	4×ρ: 0.528 $\Delta\rho$: +0.376 H: +0.031 G/ρ: 1.87 $-V/G$: 1.10		none	none

[a] For comparison, the BCP values of free adamantane: 1) C–C : $\rho=1.60$ e Å^{-3}, $\Delta\rho=-0.483$ au, $H=-0.175$ au, $G/\rho=0.230$ au, $-V/G=4.2$; 2) C–H (averages): $\rho=1.90$ e Å^{-3}, $\Delta\rho=-1.01$ au, $H=-0.298$ au, $G/\rho=0.160$ au, $-V/G=7.6$. [b] Near to Figure 5a. [c] Near to Figure 5b. [d] Near to Figure 5c. [e] Figure 5d.

At larger He distances R^*, there are the three expected He···H(^{s}C) AILs (Figure 5a), with comparatively low electron densities (ρ) and small positive Laplacians at the BCP (Table 1, upper row), which indicates some weak noncovalent interaction. When the He atom comes nearer to the cage, the AILs bend inwards and flip near $R^*\approx 2.5$ Å from the three H to the three ^{s}C atoms (Figure 5b). When He approaches the center of the C_6 entrance ring, three additional He···^{t}C AILs within the ring and one long He···^{t}C AIL to the bottom of the cage are formed (Figure 5c). The He–C electron densities are only a fraction of the C–C or C–H densities, as to be expected for Pauli-repulsive closed-shell overlaps, which are characterized by remarkably positive Laplacian values. In the eyes of chemists, the latter are often attractive (e.g., F–F or Na–Cl), but in the present case (He–CR_4) they appear repulsive. At R^*

≈ 0.6 Å, the three somewhat longer He···^{t}C AILs have disappeared, and four He···^{t}C AILs remain. They become equivalent for the equilibrium IC at $R^{*}=0$ (Figure 5d). The QTAiM interactions of He at equilibrium with four ^{t}C, and at the TS with six C atoms (three ^{t}C and three ^{s}C) are comparable with respect to ρ and $\Delta\rho$. The nearly vanishing local energy-density values of H, and the significantly positive local kinetic-energy values G/ρ of 1 to 2 au, and the bond degree ratios $-V(\mathrm{BCP})/G(\mathrm{BCP})$ of about 1.0 indicate that these interactions are neither covalent nor ionic attractive, in accordance with the chemical point of view.[39,40]

Conclusion

The description of a bonded aggregate A–B can be performed along different approaches. We have applied MZB-EDA energy partitioning of the electronic wavefunction of the bonded molecule, and QTAiM analysis of its electron-density distribution. A descriptive tool can develop into an explanative tool, if 1) appropriately chosen nonbonded reference fragments can be compared with the bonded aggregate, and if 2) the bonding energy can be partitioned in such a manner that one dominant term (or a very few terms of the same sign) can be related to a specific physical mechanism. It is the structure–energy function that characterizes the bonding.

The energy changes from the educts (here the free components) to the TS and then to the product (the IC) are qualitatively displayed in Table 2. In the case at hand, the total energy variation happens to be just of the order of the steric repulsion, $\Delta E \approx \Delta E^{o} = +\Delta E_{\mathrm{steric}}$, which is dominated by the kinetic part of the nonbonding Pauli energy increase (Figure 4). This is described by the intermediate wavefunction $\Psi^{o}_{\mathrm{overlay}}$ [Eq. (2)]. According to the virial theorem, the relaxed stationary wavefunction of the high-energy IC, $\Psi_{\mathrm{A-B}}$, yields a smaller kinetic energy, namely, $\Delta T = -\Delta E$, with $\Delta V = +2\Delta E$. In our approach, the physical origin of the endothermicity of the complex formation of the two closed-shell components is attributed to and explained by the kinetic-energy-driven Pauli repulsion (T^{o} increase), whilst the result of the complex formation corresponds to a total energy increase and a respective T decrease. The opposite holds for a typical covalence, which is driven by a reduction of the kinetic energy functional due to overlap of half-filled shells and delocalizing electron sharing. The variational principle then leads to an increased final kinetic energy value. A fully relaxed (‘correct’ stationary) wavefunction is required for reasonable expectation values of any observable (except for the variationally stable energy that can already be recovered by less accurate wavefunctions), for example, for T and V. Various approximate wavefunctions together with variational reasoning can be used to derive various physical explanations.

One may also split up the total compression energy ΔE of the IC into contributions from He (electronic compression constant k_{He}) and from adamantane (electronic and structure compression constant $k_{\mathrm{ad}} < k_{\mathrm{He}}$).[41] In the harmonic approximation, $\Delta E = \Delta E_{\mathrm{He}} + \Delta E_{\mathrm{ad}} \approx [k_{\mathrm{He}}/2(\Delta R_{\mathrm{He}})^2] + [k_{\mathrm{ad}}/2(\Delta R_{\mathrm{ad}})^2]$, with equilibrium condition $k_{\mathrm{He}}\Delta R_{\mathrm{He}} = k_{\mathrm{ad}}\Delta R_{\mathrm{ad}}$. Therefore, $\Delta E_{\mathrm{He}}/\Delta E_{\mathrm{ad}} = k_{\mathrm{ad}}/k_{\mathrm{He}} < 1$. The opposite statement that the formation energy of strained endohedral complexes is dominated by the electronic compression of the *endo* atom rather than by the stretched cage was due to some conceptual mixup in the definitions.[41]

In the case of He@adamantane, the Pauli repulsions between He and the saturated adamantane atoms are comparable for the IC and TS. The largest contribution to the decay barrier from the IC to the TS, $+\delta$, is the potential-energy increase of the additional adamantane deformation. The origin for the metastability of the IC, as already pointed out by Strenalyuk and Haaland,[2b] is the stability of the network of the C–C covalences of adamantane, which surmounts the Pauli repulsion between the closed shells of adamantane and He. According to the Pauling/IUPAC definition,[9] there is a bond between atoms if some forces keep them together. Here He and adamantane are kept together because of the bonding between the carbon atoms of adamantane.

Table 2. Qualitative energy changes: kinetic (T), potential (V), and total energy (E) of separated fragments He and adamantane, of the inclusion complex He@adamantane, and of the transition state (TS) on the barrier; for the optimized stationary states, and at the lowest-order perturbation theory [PT; Eq. (2); ΔE_{ster}, Eq. (3)]. Upper part of table: MZB-EDA; lower part: QTAiM partitioning.[a]

MZB-EDA	T	V	E
free fragments	$+F$	$-2F$	$-F$
He@adamantane (PT)	$\approx +F+\Delta E+a$	$\approx -2F-a$	$\approx -F+\Delta E$
He@adamantane (optimized)	$= +F-\Delta E$	$= -2F+2\Delta E$	$= -F+\Delta E$
TS (PT)	$\approx +F+\Delta E+b$	$\approx -2F+\delta-b$	$\approx -F+\Delta E+\delta$
TS (optimized)	$= +F-\Delta E-\delta$	$= -2F+2\Delta E+2\delta$	$= -F+\Delta E+\delta$

QTAiM	Fragments	Interaction	E
free fragments	$-F$	0	$-F$
He@adamantane	$-F+C+\Delta E$	$-C$	$-F+\Delta E$
TS	$-F+G+\Delta E+\delta$	$-G$	$-F+\Delta E+\delta$

[a] F = reference energy of the free fragments He and adamantane; ΔE = decay energy of the complex ($\approx +6.5$ eV); δ = decay barrier ($\approx +1.75$ eV); a and b are huge potential-energy lowerings due to density overlap and orbital orthogonalization, and parts of the huge kinetic-energy increases due to orbital orthogonalization ($a \approx 35$ eV, $b \approx 33.5$ eV); C = large QTAiM stabilization of the QTAiM fragments in the complex due to the electrostatic Ehrenfest forces ($\approx +14.25$ eV);[3b] G is the respective value at the TS.

Such a situation is quite common in close-packed structures, particularly in ionic lattices, in which big anions are pulled together into direct contact by small cations. Whereas the repulsion between the closed-shell anions in alkali halides and alkaline earth chalcogenides (e.g., LiF or MgO) due to the Coulomb and Pauli forces largely dominates over the attractions due to polarization and dispersion,[42] anion–anion AILs are found frequently.[43,44]

The MZB-EDA approach (for instance) can be used to attach well-defined quantum-physical meanings to the somewhat fuzzy chemical-bonding concepts that were inductively constructed out of the mass of chemical experience. Since the explanation of bonding requires the choice of a nonbonded reference, explanations must depend on the details of the chosen reference (e.g., optimized or deformed fragments; neutral or charged fragments; in the case of open shells various possible spin–orbital occupations and spin couplings). Objective fact-adapted personal choices offer complementary explanations. Such ambiguities can only be avoided if one refrains from explanations at all and confines oneself to the description of the final stationary states, for example, by applying reference-free QTAiM.[8]

Stable or metastable educts and products and the TS are defined by vanishing energy gradients, that is, by zero forces. The total energy consists of two equally relevant terms, a kinetic and an electrostatic one. If one assumes the solutions of the Schrödinger equation as given, one can eliminate one of the two. One can then represent the energy as $E=-T$ or as $E=\frac{1}{2}V$. (The reduction factor of $\frac{1}{2}$—which is only valid at an equilibrium structure—is often forgotten in purely electrostatic attempts of pseudoexplanation.) One can also represent the forces $-F=\nabla E=\nabla T+\nabla V=-F_{\text{elstat HFF}}$ as purely electrostatic effects. However, one then no longer has the chance to understand how the shape of the wavefunction comes about through the variational competition of kinetic and electrostatic repulsive and attractive energy contributions.[12,13]

In the EDA approach, the lowest-order interaction energy of overlapping closed-shell fragments is dominantly Pauli repulsion somewhat reduced by electrostatic attraction, whereas in the case of spin-paired open-shell fragments it is dominantly kinetic sharing attraction and electrostatic attraction. The final relaxation of the aggregate is more or less stabilizing.

In the QTAiM approach, the nearest neighbors, which overlap in the traditional sense, are connected by maximal electron density paths (AILs). Since there is no sufficiently accurate, variationally useful relation known between the electron density and the kinetic energy density,[45] there is no obvious relation between electron density and interatomic interaction energies. (However the situation seems to be improving.[43,46]) One can just estimate the purely electrostatic interactions between the modified fragments in the QTAiM framework, which are usually attractive. While kinetic energy and kinetic-energy density are decisive components of two-center attractions and repulsions in the EDA approach, they are defined as intrafragment contributions in the QTAiM approach.[9,18]

When the physical situation of an aggregate can be explained, for instance, with the help of the EDA approach, one can then predict qualitatively whether the fragment-modification energy of QTAiM will largely overcompensate the electrostatic QTAiM stabilization (as in the present case of He@adamantane or in ionic lattices), or not as in the case of a chemical bond. That is, the EDA approach can be used to find out whether a bond path or AIL as a bridge of density linking the QTAiM-stabilized atoms[8,45] represents a chemically bonding or antibonding interaction.[11,22] London in 1928 seems to have been the first one to distinguish between bonding and 'separating' density bridges.[47]

One must carefully distinguish between the concepts of chemical bonding (or antibonding), representable by energy increments, and QTAiM interaction, defined through density bridges.[8] This has recently been notified by Bader.[8e] Obviously, a density bridge does not automatically indicate an energetically stabilizing interaction, as sometimes conjectured.[8,44a,48] It is a common prejudice to take charge concentration or charge accumulation between nuclei as the necessary and sufficient indication of chemical bonding, without accounting for the concomitant charge depletion and charge polarization near the nuclei and a careful analysis of the changes of potential and kinetic energies. There are many examples in the literature that demonstrate the difference of 'chemical' and QTAiM interactions.[22] More investigations into the relations between the physically rigorous QTAiM concepts[53] and the fruitful, though fuzzy chemical concepts are still needed. Efforts towards the development of the descriptive QTAiM tool into an explanative tool[11,18,49] seem fruitful, in particular, if the kinetic energy density is considered, too, in addition to the charge density.

The energy values ΔE and δ in Table 2 suggest a low-energy threshold for collisions of He against adamantane at center-of-gravity energies around 7 to 10 eV. The decay barrier height is about 10 harmonic quanta of the He vibration of T_2 type, which couples with many cage vibrations, so that both tunneling and above-barrier formation of a weakly warmed up IC should be possible in brute-force collision experiments.[50] The decay barrier is high enough to guarantee a long lifetime for low vibrational states.

Acknowledgements

We thank, first of all, Klaus Ruedenberg for his papers and personal discussions, which guided us to our philosophical insights into chemical bonding. We also thank our colleagues P. Ayers, M. Bickelhaupt, J. Cioslowski, G. Frenking, S. Grimme, A. Haaland, D. Jayatilaka, A. Martín-Pendás, G. Merino, P. Popelier, S. Shahbazian, M. Solà, and the unknown referees for many illuminating and improving comments. We acknowledge financial support by the National Nature Science Foundation of China (nos. 20773086 and 20973109).

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[51] Originally, bond paths were defined (for basic theoretical reasons of the definition of atoms in molecules) only at the stationary points of the molecular PES at the nonrelativistic and lowest-order BO approximation.[8a] Any real molecular structure is, however, the expectation value over the zero point or thermal vibrational distribution on the PES around the stationary points. We do not know of any convincing argument as to why the bond-path concept should be inapplicable to any real stationary or intermediate structure. Yet, we will use the term atomic interaction line (AIL), instead of bond path, for the electron-density bridges between the nuclei.

[52] a) S. F. Boys, F. Benardi, *Mol. Phys.* **1970**, *19*, 553; b) F. B. van Duijneveldt, J. G. C. M. van Duijneveldt-van de Rijdt, J. H. van Lenthe, *Chem. Rev.* **1994**, *94*, 1873.

[53] Note added in proof (June 23, 2010): There just appeared an extended review of the Bader model of bonding by R. F. W. Bader in *J. Chem. Phys. A* **2010**, ASAP online June 15, 2010 (DOI: 10.1021/jp102748b) It maintains that *all* possible facets of bonding are considered, however, dismissing the chemically relevant differences between “ionic, polar, covalent, hydrogen bonded, van der Waals”, nonbonding and other interactions. It is noted, for instance, that “there is no physical distinction between the bond paths linking cations to anions and those linking anions to anions or cations to cations”, in the Bader model of bonding. The paper does not contribute new aspects to the field discussed here.

Received: March 29, 2010