Topological Analysis of Electron Densities: Is the Presence of an Atomic Interaction Line in an Equilibrium Geometry a Sufficient Condition for the Existence of a Chemical Bond?

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Abstract: The structure, energetics, and electron density in the inclusion complex of He in adamantane, $C_{10}H_{16}$, have been studied by density functional theory calculations at the B3LYP6-311++G(2p,2d) level. Topological analysis of the electron density shows that the He atom is connected to the four tertiary ${}^{t}C$ atoms in the cage by atomic interaction lines with (3,−1) critical points. The calculated dissociation energy of the complex He@adamantane(g) = adamantane(g) + He(g) of $\Delta E = -645\ \mathrm{kJ\,mol^{-1}}$ nevertheless shows that the He–^{t}C interactions are *antibonding*.

Keywords: bond energy · bond theory · charge density · density functional calculations · inclusion compounds

Introduction

The elegant methods for topological analysis of electron densities, "Atoms in Molecules" or AIM, developed by Bader and co-workers have provided chemists with a valuable tool for examination and description of chemical bonding in molecules or solids;[1,2] according to the ISI Web of Science the research literature contains nearly 2000 references to Bader's monograph[1] since its publication in 1990. This paper, however, is concerned with an aspect of AIM that has been controversial.

The first step in the topological analysis consists of locating all critical points (CPs) on the three-dimensional electron density surface $\rho(\boldsymbol{r})$, that is, all points where the gradient of the electron density is zero [Eq. (1)].

$$\nabla\rho(\boldsymbol{r}) = \boldsymbol{i}(\partial\rho/\partial \mathrm{x}) + \boldsymbol{j}(\partial\rho/\partial \mathrm{y}) + \boldsymbol{k}(\partial\rho/\mathrm{d}z) = 0 \qquad (1)$$

Critical points are then classified by calculating the Hessian matrix of the electron density, that is, the nine second derivatives of type $\partial^2\rho/\partial q_i\partial q_j$, and diagonalizing it. If all the diagonal elements are negative, the CP represents a local *maximum* of the electron density. Such maxima, "attractors", are found at or near the nuclei of all atoms in the molecule. If all the diagonal elements are positive, the CP represents a local *minimum* or a "cage" CP. Critical points for which two elements in the diagonalized Hessian are positive and one negative are referred to as (3,+1) or "ring" CPs. They represent *saddle points* on the three-dimensional $\rho(\boldsymbol{r})$ surface: the electron density increases in two and decreases in the third, perpendicular direction.

Finally CPs for which one element in the diagonalized Hessian is positive while two are negative are referred to (3,−1) or "bond" CPs. These points also represent *saddle points* on the $\rho(\boldsymbol{r})$ surface: the electron density increases in one direction and decreases in all directions perpendicular to it. A (3,−1) CP is generally found at or near the axis connecting the two nuclei of each bonded atom pair. A line beginning at the CP and following a path of steepest ascent (increase) of electron density will end at one of the two nuclear attractors. The two atoms are thus connected by a line following a ridge of accumulated electron density between the nuclei. Such lines are referred to as *atomic interaction lines* (AILs). Finally the boundary surface between the two atoms is defined as containing all lines of steepest descent from the (3,−1) CP obtained by first making an infinitesimal displacement from the CP in a direction perpendicular to the AIL.

Is the existence of an atomic interaction line sufficient to prove that the two atoms are joined by a chemical bond in

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the accepted sense of the word? Most chemists would probably agree that the defining property of a chemical bond is the existence of a positive bond rupture energy, that is, that the energy of the molecule is lower than the energy of the fragments, and this is the definition adopted in this paper. Bader argues the point in general terms: "Both theory and observation concur that the accumulation of electronic charge between a pair of nuclei is a necessary condition if two atoms are to be bonded to one another. This accumulation of charge is also a sufficient condition when the forces on the nuclei are balanced and the system possesses a minimum energy equilibrium internuclear separation".[3] This "sufficient and necessary condition" postulate does indeed appear plausible, but has never been proven.

The presence of an atomic interaction line between the nuclei of atoms A and B shows that there is an accumulation of negative charge between them, but this accumulation is not necessarily large enough to overcome the Coulomb repulsion between the positively charged nuclei. Such is clearly the case for a pair of noble gas atoms at close range; calculations show that the atoms are connected through an AIL even if the interaction is strongly repulsive. Consider a molecule consisting of two fragments joined by *one* AIL between atoms A and B. If the structure of the molecule corresponds to a minimum on the energy surface, it will require energy to separate the two fragments; in this case the additional condition that the structure represents a minimum on the energy surface is sufficient to assure that the interaction between A and B is bonding. Similarly, if a molecule consists of two fragments joined by *two* AILs, say between atoms A and B and between C and D, it will normally be possible to break the interaction between atoms A and B by rotating the two fragments about the C–D axis. In this case, too, the additional condition that the molecule is in a minimum on the energy surface is sufficient to assure that the interaction between A and B is bonding. If, however, a molecule consists of two fragments connected through *three or more* AILs, the structure and rigidity of the molecular frame may make it impossible to break the interaction between nuclei A and B without breaking some of or all the other AILs in the process. Under such circumstances it will be possible to determine the A−B bond energy only if all the broken AILs are symmetry equivalent. If they are not, the A−B bond energy cannot be determined and a chemical bond between A and B remains—strictly speaking—an undefined concept.

Cioslowsky and co-workers have investigated a number of organic molecules commonly believed to be destabilized through steric strain, that is, through repulsion between nonbonded atoms at short internuclear distances imposed by the structure and rigidity of the molecule.[4] Since topological analyses of the electron densities revealed atomic interaction lines between the atoms purported to repel each other, Cioslowsky and Mixon concluded that the existence of an AIL "does not necessarily imply the presence of bonding between the nuclei" but should be interpreted as indications for "either bonding or nonbonding, attractive or repulsive" interactions.[4a]

More recently Tsirelson and co-workers have analyzed accurate, experimentally determined electron densities in crystals of LiF, NaF, and NaCl.[5] As expected each anion was found to be connected to six nearest neighbor cations, and each cation to the six nearest anions, through AILs with (3,−1) CPs. Somewhat unexpectedly, however, each anion was also found to be similarly connected to twelve second-nearest neighbor *anions*. Similar results have been obtained by analysis of calculated intensities.[5a,6] All alkali metal halides except CsCl, CsBr, and CsI crystallize with a rock salt lattice. Pendás and co-workers have calculated the electron densities in each and found AILs between the anions in all but six of them: anion–anion AILs appear to be favored when large anions are combined with small cations.[6b] Since it is impossible to break an anion–anion interaction line without breaking several anion–cation interactions in the process, the energy required to break an anion–anion AIL cannot be determined. Strong indirect evidence suggests, however, that the crystals are strongly destabilized by the electrostatic anion–anion interactions; the anion–anion interaction energies calculated from the experimental charge densities in LiF and NaF are greater than 400 kJ mol^{-1}.[7] Yet, according to the "sufficiency postulate", the presence of the AILs implies that the anions are bonded to one another.

The results obtained in the studies of alkali metal halides led Tsirelson and co-workers to question "whether one can consider the existence of a (3,−1) critical point on the line between atoms as a sign of bonding",[5a] while Abramov suggested that the appearance of AILs "is quite possible for crystals formed from ions with noticeable different sizes" even in the absence of bonding interactions.[7a]

In a response published in 1998 Bader[8] stressed that the only valid description of the electrons and nuclei in a molecule is that provided by quantum mechanics. When a molecule is in an equilibrium geometry there are no net forces acting on an element of the electron density, nor on the nuclei. A displacement of the nuclei from their equilibrium positions induces forces that are so directed as to reestablish the equilibrium geometry. "That standard geometrical parameters are changed [–] does not imply the presence of repulsive forces in the final equilibrium geometry". He therefore rejected interpretations in terms of "repulsive interactions" or "repulsive forces" acting on atoms in molecules or "electrostatic repulsive interaction" between halide anions in crystals. In conclusion he reasserted that for a system in a stationary state, the presence of an AIL between two atoms is "sufficient for the two atoms to be bonded to one another in the usual chemical sense of the word", and this view appears to have become widely accepted.[9]

It occurred to us that an endohedral complex of a rare gas atom in a small hydrocarbon cage, for instance that of He encapsulated in adamantane, might provide a simple and clear-cut test of the "sufficiency postulate". If the rare gas atom is large enough its interactions with the carbon atoms in the cage would be strongly destabilizing, but the endohedral complex might nevertheless correspond to a minimum on the energy surface if the cage is sufficiently rigid to provide a barrier to dissociation. At the same time the bonding or antibonding character of the interactions between the rare gas and the C atoms could be determined directly by comparing the energy of the complex with those of the separated constituents.

Results and Discussion

The van der Waals' radii of the He atom[10] (296 pm) and the spherically averaged methane molecule[11] (402 pm) suggest that the interaction energy should be positive for distances smaller than about 320 pm. We have studied the interaction by optimizing the structure of He·CH_4 dimers under C_{3v} symmetry with fixed He···C distances ranging from 320 to 160 pm. As expected, the interaction energies are positive and increase exponentially with decreasing distance (Table 1). The He·C Mulliken overlap populations are all negative as expected for antibonding interactions, and vary from −0.006 at He···C = 320 pm to −0.279 at He···C = 160 pm. Topological analyses of the calculated electron densities show that the He and C atoms are connected by an AIL with a (3,−1) CP. The electron density at the CP, $\rho(\boldsymbol{r}_c)$, increases with decreasing He···C distance, and the Laplacean of the density at the CP, $\nabla^2\rho(\boldsymbol{r}_c)$, is positive as expected for closed-shell interactions.[1]

Table 1. Interaction energies of He·CH_4 dimers of C_{3v} symmetry (ΔE) as a function of the He···C distance. Total electron density and the Laplacian of the density at the critical point on the He···C interaction line.

R(He···C) [pm]	ΔE [kJ mol^{-1}]	$\rho(\boldsymbol{r}_c)$ [au]	$\nabla^2\rho(\boldsymbol{r}_c)$ [au]
∞[a]	0.0	0.0	0.0
320	0.7	0.002	0.010
280	2.3	0.005	0.027
240	10.6	0.013	0.072
200	47.2	0.031	0.172
160	190.4	0.076	0.380

[a] E(He) = −2.913544 au and $E(CH_4)$ = −40.536693 au.

The molecular symmetry of adamantane (*adam*), $C_{10}H_{16}$ or $(CH)_4(CH_2)_6$, is T_d (Figure 1). In the following we shall denote the four tertiary C atoms by ^{t}C, and the six secondary C atoms as ^{s}C. The molecular structure of the C_{10} frame is determined by just two parameters, the ^{t}C–^{s}C bond length and the ^{t}C-^{s}C-^{t}C valence angle. Specification of the positions of the H atoms requires three more parameters, namely the two bond lengths ^{t}C–H and ^{s}C–H, and the H-^{s}C-H valence angle. DFT structure optimization yielded the bond lengths and valence angles listed in Table 2. Calculation of the molecular force field confirmed that this structure represents a minimum on the energy surface. The equilibrium ^{t}C–^{s}C bond lengths and ^{t}C-^{s}C-^{t}C valence angles are in excellent agreement with the thermal average values determined by gas electron diffraction, r_a = 154.0(2) pm and θ_a = 109.8(5)°, respectively.[12] Topological analysis of the electron density leads to the identification of (3,−1) critical points and AILs between all bonded C–C or C–H atom pairs, four (3,+1) ring CPs and one cage (3,+3) CP at the center (Figure 2 and Table 3). The electron densities in the bond critical points as well as the large, negative values of $\nabla^2\rho(\boldsymbol{r}_c)$ are as expected for covalent, electron-sharing bonds.[1]

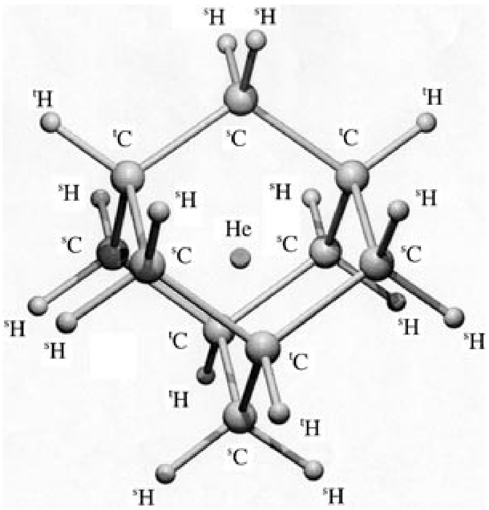

Figure 1. Molecular structure of the endohedral complex He@*adam*, symmetry T_d.

Table 2. Relative energies (ΔE), interatomic distances, and valence angles in *adam* (optimized structure), adam* (frozen in the structure in optimized He@*adam*), He@*adam* (optimized structure), [He@*adam*]* (with *adam* frozen in the structure of the free molecule), and in the transition state for the dissociation reaction, [He@*adam*]†.

	adam[a,b]	*adam**[c]	He@*adam*[a,d]	[He@*adam*]*[d]	[He@*adam*]†[d,e]
ΔE [kJ mol^{-1}]	0.0	63.6	644.9	715.6	171.6
He···^{t}C [pm]	–	–	162.1	154.3	163.2
He···^{s}C [pm]	–	–	184.4	177.7	165.8
^{t}C–^{s}C [pm]	154.0	160.5	160.5	154.0	170.2
^{t}C-^{s}C-^{t}C [°]	109.7	111.1	111.1	109.7	110.3[f]
^{t}C–H [pm]	109.3	109.3	109.3	109.3	109.2
^{s}C–H [pm]	109.4	109.3	109.3	109.4	109.2[g]
H-^{s}C-H [°]	106.9	107.0	107.0	106.9	108.2

[a] Optimized structure. [b] E(*adam*) = −390.838989 au. [c] Energy relative to optimised *adam*. [d] Energy relative to optimized *adam* plus He atom at infinite distance. [e] The interatomic distances and valence angles pertain to the symmetry-unique $(^tCH)_3(^sCH_2)_3$ ring. [f] ^{s}C-^{t}C-^{s}C = 113.0°. [g] Average value.

A helium atom was then placed at the center of the adamantane cage and the complex optimized under T_d symmetry.[13] The structure parameters thus obtained are listed in Table 2. Calculation of the molecular force field confirmed that the optimized structure represents a minimum on the potential energy surface. Topological analysis of $\rho(\boldsymbol{r})$ shows that the He atom interacts with the four ^{t}C atoms through electron density ridges with (3,−1) CPs, but does not share boundary surfaces with the ^{s}C atoms. The $\nabla^2\rho(\boldsymbol{r}_c)$ is large positive as expected for closed shell interactions.[1]

Combination of the energy of optimized He@*adam* with the energies calculated for the free *adam* molecule and the isolated He atom yields a *negative* dissociation energy [Eq. (2)], which in turn gives a negative He·^{t}C mean bond energy of −161 kJ mol^{-1}; the interaction is *antibonding*.

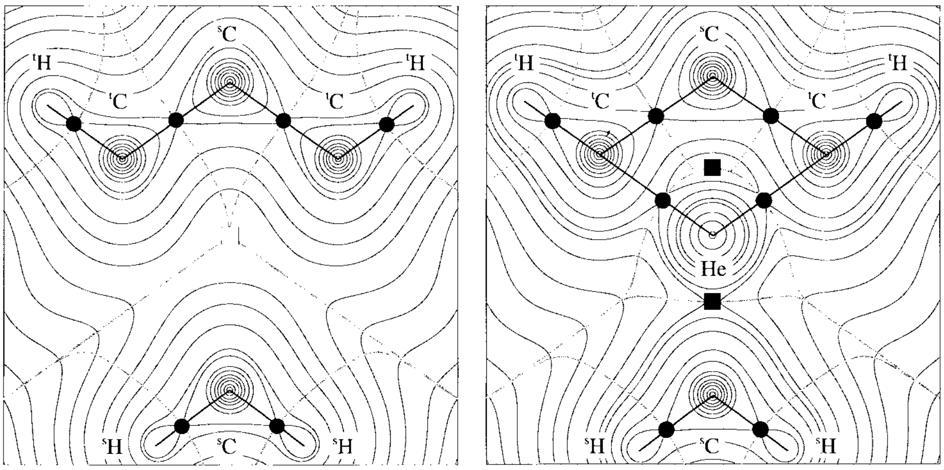

Figure 2. Calculated electron density in a molecular symmetry plane of free adamantane (left) or He@*adam* (right). Contour levels have been drawn at $\rho(\boldsymbol{r}) = 2\times10^{n}$, 4×10^{n}, and 8×10^{n} eÅ^{-3}, $n = 0, \pm1, \pm2$, or -3. Contours at 0.4(He@*adam*) and 2.0 eÅ^{-3} have been deleted and extra contours added at 1.58(*adam*), 0.39, 0.52, 1.40(He@*adam*), and 1.90 eÅ^{-3}. AILs are indicated by thick black lines, (3,−1), (3,+1), and (3,+3) CPs by closed circles, closed squares, and open squares, respectively; and AIM partitioning of the total electron density by thick gray lines.

Table 3. Critical point parameters in He·CH$_4$, *adam*, He@*adam*, and in the transition state for dissociation of the complex, [He@*adam*]†.

Distances from attractors [pm]		$\rho(\boldsymbol{r}_c)$ [au]	$\nabla^2\rho(\boldsymbol{r}_c)$ [au]
He·CH$_4$[a]			
He···C	71.0–91.1	0.073	0.365
adam			
^{t}C–^{s}C	76.9–77.2	0.237	−0.483
^{t}C–H	68.5–39.2	0.283	−1.021
^{s}C–H	68.6–39.3	0.281	−1.003
rings[b]		0.020	0.113
cage		0.012	0.077
He@*adam*			
He–^{t}C	72.1–90.0	0.078	0.362
^{t}C–^{s}C	80.2–80.3	0.211	−0.362
^{t}C–H	68.9–38.8	0.284	−1.036
^{s}C–H	68.7–38.9	0.282	−1.010
rings[c]		0.059	0.305
[He@*adam*]†[d]			
He–^{t}C	71.9–91.5	0.078	0.365
He–^{s}C	72.4–93.7	0.076	0.358
^{t}C–^{s}C	84.9–85.3	0.177	−0.238
^{t}C–H	69.1–38.6	0.284	−1.035
^{s}C–H[e]	69.0–38.7	0.282	−1.018

[a] He···C fixed at 162.1 pm. [b] Four six-membered rings $^{t}C_3{}^{s}C_3$. [c] Six four-membered rings He^{t}C$_2{}^{s}$C. [d] The parameters pertain to the symmetry-unique (^{t}CH)$_3$(^{s}CH$_2$)$_3$ ring. [e] Average values.

$$\text{He@}adam = \text{He} + adam,\ \Delta E_{\text{dis}} = -645\,\text{kJ}\,\text{mol}^{-1} \quad (2)$$

The large negative He·^{t}C Mulliken overlap populations, −0.33 as compared to −0.26 obtained for the He·CH$_4$ dimer at the same He···C distance, are consistent with this description. It is also noteworthy that the topological parameters of the He···^{t}C interactions are very similar to those calculated for the He·CH$_4$ dimer at the same He·C separation (Table 3).

The dissociation reaction may be divided into two steps; the first involves dissociation of the complex to yield a He atom and an *adam* molecule with unaltered structure, the second the geometrical relaxation of the hydrocarbon cage. The first step is strongly exothermic: $\Delta E^{*} = -581$ kJ mol^{-1}. The major part of the energy released is due to elimination of the He···^{t}C interactions, only 10% are due to the subsequent relaxation of the hydrocarbon frame.

Formation of the complex may also be divided into two steps; the first involves the introduction of the He atom without change of cage structure, the second the geometrical relaxation of the inclusion complex. The energy of a complex obtained by placing the He atom in the center of the unaltered cage determined by a single-point calculation, is 716 kJ mol^{-1} above that of the separated constituents. The distance from the He atom to the ^{t}C atoms is He·^{t}C = 154.3 pm, and the average He·^{t}C interaction energy, 179 kJ mol^{-1}, is comparable to the interaction energy calculated for the He·CH$_4$ dimer at the same He···C distance, 230 kJ mol^{-1}. This structure does not correspond to a minimum on the energy surface, there are forces acting on the ^{t}C nuclei pushing them away from the He atom at the center. Structure optimization of the complex leads to an expansion of the cage and the He···^{t}C distances increase by about 8 pm. This is accomplished by an elongation of the ^{t}C–^{s}C bonds from 154.0 to 160.5 pm and by an opening of the ^{t}C-^{s}C-^{t}C angle from 109.7° to 111.1°. At the same time the energy of the complex falls by 71 kJ mol^{-1}.

The energy of a free adamantane molecule with the structure adopted in the complex (*adam**) is 64 kJ mol^{-1} above that of the equilibrium. Due to the elongation of C–C bonds and opening of CCC valence angles there are forces acting on all nuclei to restore the equilibrium geometry. The resultant force on the ^{t}C nuclei is pulling them back towards the center of the cage. As pointed out by Bader,[8] there are no *net* forces acting on the atomic nuclei when the inclusion complex is in the equilibrium conformation; the forces pushing the ^{t}C atoms away from the He atom at the center of the cage have been balanced by forces pulling them back. Though there are no net forces acting on the nuclei, the complex is destabilized, primarily by ^{t}C···He repulsive interactions and to a lesser extent through the strain induced in the ligand.

The atomic energies and net atomic charges calculated by integration over the atomic volumes are listed in Table 4.[14] Since the He···^{t}C interactions are antibonding, we were surprised to find that the energy of the He atom in the complex is 1263 kJ mol^{-1} *lower* than that of the free atom. The reason for this apparent contradiction is probably that the shape of the He atom which is removed in the dissociation process is very different from that of the He atom obtained by topo-

Table 4. Atomic energies and net atomic charges in *adam* and He@*adam*.

	adam		He@*adam*	
	$E(\Omega)$[a] [au]	$q(\Omega)$ [au]	$\Delta E(\Omega)$[b] [kJ mol^{-1}]	$q(\Omega)$ [au]
^{t}C	−38.0432	0.063	218	0.076
^{s}C$_s$	−38.0518	0.057	137	0.046
^{t}H	−0.6513	−0.037	16	−0.033
^{s}H	−0.6462	−0.038	13	−0.031
He	–	–	−1263[c]	−0.085

[a] Absolute energy. [b] Relative energy. [c] Relative to free He atom.

logical analysis with its four surfaces at which the electron density drops abruptly to zero: Comparison of the electron density of *adam* and with that of He@*adam* (Figure 2) shows that the electron density inside the AIM boundary surfaces of the He atom has not not fallen to zero, and that the electron density outside the boundaries has been perceptibly reduced.

The adamantane molecule may be described as consisting of four fused six-membered rings formed by alternating ^{t}C and ^{s}C atoms. In order for the complex to dissociate, the He atom must exit through one of these rings, but is too large to pass unhindered. The height of the resulting barrier to dissociation was determined by optimizing models under C_{3v} symmetry in which the He atom were displaced from the center towards the symmetry-unique C_6 ring. The transition state was found for a model where the He atom was within 0.5 pm of the plane defined by the midpoints of the six ^{t}C–^{s}C bonds, the He–^{t}C and He–^{s}C distances being 163.2 pm and 165.8 pm, respectively. Topological analysis showed that the He atom was connected to each of the six ring C atoms through an AIL. The ^{t}C–^{s}C bond lengths in the ring had increased to 170.2 pm, and the energy of the transition state was 172 kJ mol^{-1} above that of the optimized endohedral complex. Calculation of the vibrational frequencies yielded one totally symmetric imaginary mode, $\omega = 986i$ cm^{-1}, in which the He atom is constrained to move along the threefold symmetry axis.

Concluding Remarks

We have shown that even though the He atom in the inclusion complex He@*adam* is connected to the four tertiary C atoms through atomic interaction lines with (3,−1) critical points, the He···^{t}C interactions are in fact strongly antibonding. This means that the conjecture that an AIL between two atoms in an equilibrium structure implies the presence of a chemical bond between them is *not valid*. Up to the present the overwhelming majority of the atomic interaction lines found in molecules subjected to AIM topological analysis of electron densities clearly correspond to bonding or stabilizing interactions. We do not doubt that this trend will continue into the future. But, since the results reported in this article show that AILs *may* indicate destabilizing or antibonding interactions, the interpretation must in each case be judged on its merits.

Methods

Structure optimization by DFT calculations were carried out using the GAUSSIAN 98 program package, with the B3LYP functional and a standard 6-311++G(2p,2d) basis set for all atoms.[15] Topological analyses of calculated electron densities were carried out partly with GAUSSIAN and partly with the AIMPAC software package.[14]

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