Ab initio MO calculation on the energy barrier for the penetration of a benzene ring by a helium atom. Model studies for the formation of endohedral He@$C_{60}^{+\cdot}$ complexes by high-energy bimolecular reactions

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Ab initio MO calculations are reported for the C_{3v}-symmetric penetration of C_6H_6 and $C_6H_6^{+\cdot}$ by a helium atom. At the highest level of theory (MP2/6-31G**//MP2/3-21G*) barriers of 10.7 and 9.4 eV are obtained. The calculated binding energy of a helium atom to benzene is negligible. These computational results are in agreement with recent experiments on the successful formation of endohedral He@$C_{60}^{+\cdot}$ complexes and may contribute to the understanding of the penetration mechanism of fullerenes in high-energy bimolecular reactions in the gas phase.

1. Introduction

The emptiness of fullerenes C_x begs the question whether it is possible to lock atoms (or molecules) M into the cage and so to produce new *endohedral* compounds for which the symbol M@C_x has been recommended [1]. Although there are various theoretical examinations of the properties of inclusion compounds [2–8], examinations of the mechanism of formation are rare. Bakowies and Thiel [6] have performed MNDO-calculations for the exo/endo migration for several Li@C_x^+ complexes and so have shown that the penetration of a hexagon requires considerably less energy than that for pentagons (7.2 versus 10.2 eV). However, recent large-scale ab initio MO calculations by Cioslowski [8] show that MNDO is incapable of predicting properties of endohedral complexes correctly. Extensive molecular dynamics simulations of the penetration of $C_{60}^{+\cdot}$ by He atoms have also been performed [9] and, aside from many other interesting findings, the perpendicular approach towards the face of a hexagon was obtained as the preferred direction for penetration. 9.35 eV was obtained for the activation energy. The authors calculated a barrier of 13.1 eV for the analogous reaction through the centre of a pentagon of C_{60}.

Indeed, experiments performed first in our laboratory [10–15] and later by other research groups [9,16–20] have shown unequivocally that endohedral noble-gas fullerene complexes N@C_x^{n+} for combinations of N=He, Ne, Ar, $x=60$, 70 and $n=1$, 2, 3 can be produced by bimolecular high-energy collisions of the type

$$C_x^{n+} + N \rightarrow [N@C_x^{n+}]^{**} \rightarrow [N@C_{x-m}]^{+} + C_m \quad (m=2, 4, ...) . \qquad (1)$$

A number of independent experiments have revealed that the noble gas in adducts obtained in this manner is found inside the cage and not glued to the outer surface, as is the case with the $MC_{60}^{+\cdot}$ complexes (M=Fe, Co, Ni, Rh, La, VO) generated by

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thermal ion/molecule reactions [21–23]. The definitive proof that $HeC_{60}^{+\cdot}$ is an endohedral complex $He@C_{60}^{+\cdot}$ was obtained recently in that it was possible to reduce $HeC_{60}^{+\cdot}$ to *neutral* HeC_{60} by electron transfer in a molecular-beam experiment and to reionize this compound to $HeC_{60}^{+\cdot}$ after ≈90 μs in a spacially and temporally separate experiment [15]. The onset energy for the reaction of $C_{60}^{+\cdot}$ with He and Ne required for penetration is 6 ± 2 and 9 ± 1 eV, respectively, according to the most recent values available [19].

Our initial ab initio MO calculations predicted, in good agreement with Campbell's data, that the barrier for the penetration of a hexagon by helium should be less than 10 eV, and that the barrier for neon, which is incorporated into $C_{60}^{+\cdot}$ with a distinctly lower effective cross section, should be ≈2 eV higher [11,14]. Here we discuss our ab initio MO calculations for the penetration of the hexagonal surface of benzene and its radical cation by a helium atom, which can serve as a model for the penetration of fullerenes. The exclusion of the pentagon is justified to the extent that it definitely has a smaller diameter (2.20 Å) than that of a hexagon (2.82 Å); the van der Waals radius of helium itself is 1.4 Å.

2. Computational details

All calculations were performed with the GAUSSIAN 90 program [24] using the 3-21G* [25] and 6-31G** basis sets [26]. The geometries were optimized using C_{3v} symmetry at the UHF and the correlated MP2 levels [27,28].

3. Results and discussion

Fig. 1 shows a typical dependence of the energy required to penetrate C_6H_6 for the approach of He towards the centre of the benzene ring in C_{3v} symmetry. The reaction coordinate r was varied stepwise with simultaneous UHF-optimization of all remaining geometric parameters a, b and c and while keeping the benzene ring planar. The repulsive interaction already begins at the relatively large separation of 2.05 Å and rises sharply as r is decreased further. The small stabilization of the He/C_6H_6 system (<0.1 eV) relative to the completely separated components calculated at the 3-21G*//3-21G* level is presumably determined by the basis set. Both bond lengths a and b of the hexagon increase as r is decreased further. The restrictions for the optimization of geometry were removed at the energy maximum ($R=0$ Å) where the structure was completely optimized (see table 1). An analysis of the force-constant matrix indicates a transition structure (one and only one negative eigenvalue). The appropriate frequency (-1151 cm^{-1}) corresponds to an "out-of-plane" vibration of the helium atom. The results of the geometry optimization together with the activation energy for the penetration, E_0, are summarized in table 1.

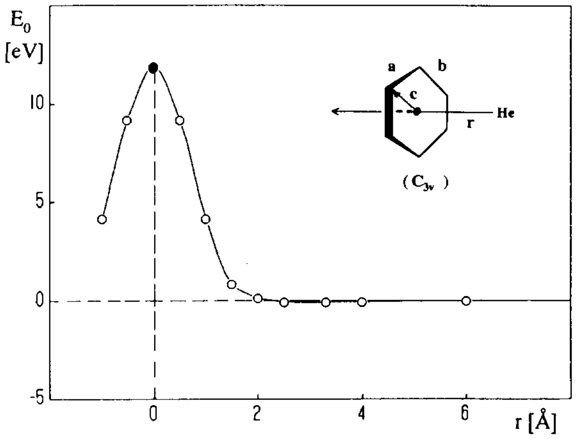

Fig. 1. Energy profile for the C_{3v}-symmetric approach of a helium atom to the centre of a benzene ring (3-21G*//3-21G*; $^1A_1$-state).

The energy for penetration for the neutral system He/C_6H_6 is reduced to 10.7 eV, and for $He/C_6H_6^{+\cdot}$ to 9.4 eV, as the basis set is enlarged and the effects of electron correlation are taken into account. These results establish good qualitative agreement with the experimental results of Campbell et al. [19], and on the basis of this trend, we expect that the barrier is reduced further as the level of theory is improved.

The model used for He/C_6H_6 can be carried over to the analogous Ne system only in a restricted fashion. More severe problems arise in the SCF convergence as the geometry of Ne/C_6H_6 is optimized. In fact, the calculations result in the dissociation of C_6H_6 into three acetylene units. A complete bond rupture

Table 1
Activation energy, E_0, for the C_{3v}-symmetric penetration of C_6H_6 and $C_6H_6^{+\cdot}$ (in parentheses) by a helium atom, and geometric data of the transition structure

	3-21G*//3-21G*	MP2/3-21G*//3-21G*	MP2/6-31G**//MP2/3-21G*	MP2/6-31G**//MP2/3-21G*
$He+C_6H_6$	−231.798293	−232.382148	−233.989699	−233.992100
$(He+C_6H_6^{+\cdot})$	(−231.519505)	(−232.027246)	(−233.625021)	(−233.634009)
E_0 (eV)	12.4 (11.8)	11.2 (10.0)	10.7 (9.7)	10.7 (9.4)
a (Å)	1.443 (1.544)	1.554 (1.509)	1.443 (1.544)	1.544 (1.509)
b (Å)	1.612 (1.627)	1.557 (1.631)	1.612 (1.627)	1.557 (1.631)
c (Å)	1.528 (1.574)	1.555 (1.542)	1.528 (1.574)	1.555 (1.542)

of this kind is probably prevented by the structure of the fullerene cage so that penetration with Ne can be achieved in the experiments with C_{60}.

An analysis of the He–C_{60} binding energy, BDE(He–C_{60}), is also important in a discussion of the experimental results, viz. the question of whether an *endo-* or *exo-hedral* structure applies for the $HeC_{60}^{+\cdot}$ complex. Our results indicate that He is very weakly bound to benzene with 591 cm^{-1} (experiment 39–43 cm^{-1} [30]) at the equilibrium separation $r=3.657$ Å (experiment 3.44 Å [29]) at the MP2/6-31G**//MP2/3-21G* level of theory. This bond energy is comparable to the vibrational frequencies of the C_{60} skeleton (528, 577, 1183 and 1402 cm^{-1} [31]). Apparently thermal energy would already be sufficient to split off an *exohedral* He atom from C_{60}. The existence of a neutral molecule $C_{60}He$ with a lifetime exceeding 90 μs has been demonstrated experimentally through the neutralization/reionization of $C_{60}He^{+\cdot}$ produced in high-energy collisions of $C_{60}^{+\cdot}$ with He [15]. Moreover, the $C_{60}He^{+\cdot}$ complexes activated in this way lose C_m fragments ($m=2, 4, 6, ...$) in the course of the break-up of the cluster cage with retention of the noble gas [10–18], although 4–5 eV is already required in the loss of C_2 from $C_{60}^{+\cdot}$ [32–34]

$$He@C_{60}^{+\cdot} \nrightarrow He+C_{60}^{+\cdot}\,,$$

$$He@C_{60}^{+\cdot} \rightarrow [He@C_{60-m}]^{+\cdot}+C_m \quad (m=2, 4, 6, ...)\,. \qquad (2)$$

The formation of the endohedral complex $He@C_{60}^{+\cdot}$ from the bimolecular reaction of $C_{60}^{+\cdot}$ with He at high collision energies is now beyond reasonable doubt. The energy required for the penetration of the cage (experiment 6±2 eV; model calculation 9.4 eV) is provided by the centre-of-mass energy of the collision.

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