An *ab initio* Hartree-Fock Investigation of Endohedral Sc@C_{82}

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The electronic structure of endohedral Sc@C_{82} with a C_{82} cage of C_{2v} symmetry has been studied by *ab initio* Hartree-Fock (HF) calculations. The optimized position of Sc in the configuration of minimum energy is predicted to be on the two-fold axis of the fullerene cage. In the corresponding configuration Sc is above the center of a hexagon of site symmetry C_2. This structure of C_{2v} symmetry is nearly degenerate with C_s and C_1 structures with Sc slightly displaced from the center of the coordinated hexagon. The binding energy of the endohedral complex is larger than 3.55 eV. The *ab initio* HF data of the C_{2v} topoisomer of the fullerene unit are compared with new experimental findings and HF results derived for the 3(C_2) topoisomer of the C_{82} cage.

Key words: Endohedral Fullerenes; Electronic Structure; *ab initio* Calculations.

1. Introduction

Endohedral metallofullerenes (MEF) have attracted much attention from experimentalists and theoreticians. One of the major challenges was the determination of the cage structure, i. e., the topology of six and five membered rings in the carbon cage, which is most frequently realized in nature under the conditions of arc discharge synthesis. In the case of C_{82}, which seems to form the most stable MEF, nine topoisomers obeying the "isolated pentagon rule" can in principle exist. A clear discrimination would require high-resolution X-ray spectroscopy or in the case of diamagnetic MEF, the evaluation of ^{13}C NMR spectra, both of which can only be performed in exceptional cases. Obviously, the availability of a quantum chemical procedure of predictive power would be of interest.

Experimental studies of M@C_{82} systems (M = Sc, Y, La) have shown that the position of the endohedral atom M is strongly off-center. This structural information has been extracted from X-ray powder [1], extended X-ray absorption fine structure (EXAFS) [2] and two-dimensional (2D) EPR [3] investigations. The experimental efforts on endohedral fullerenes have been accompanied by electronic structure investigations in different degrees of sophistication [4 - 12]. In recent publications we have presented the results of *ab initio* Hartree-Fock (HF) calculations of Y@C_{82} [8] and Sc@C_{82} [9, 10]. In the corresponding studies we have adopted a C_{82} cage of C_2 symmetry. According to the nomenclature of Manolopoulos et al. [13], the C_{82} topoisomer we have considered is denoted as 3(C_2). Our choice of the C_{82} cage geometry had been guided by the relative energies calculated for the nine topoisomers of the bare C_{82} molecule with isolated pentagons [4]. In the series of nine C_{82} topoisomers the 3(C_2) form is lowest in energy. The *ab initio* calculations of Y@C_{82} and Sc@C_{82} reported in [8 - 10] predicted an off-center position of the endohedral atom above the central 6-6 bond of a pyracylene unit in the pocket region of the 3(C_2) cage of C_{82}. The coordination number of the metal atom is six.

Results of a new X-ray investigation of Sc@C_{82} have been reported at the Meeting of the Electrochemical Society in Paris 1997 [14]. Diffraction data of improved quality have been interpreted in terms of a C_{2v} cage symmetry with Sc located on the two-fold axis above the center of a C_{82} hexagon. Stimulated and challenged by this new experimental observation we decided to extend our *ab initio* investigations of Sc@C_{82} from the 3(C_2) to the C_{2v} topoisomer of the fullerene cage. In the present concise manuscript we summarize the computational findings for the C_{2v} topoisomer of Sc@C_{82} and compare these results with our findings for the 3(C_2) pendant.

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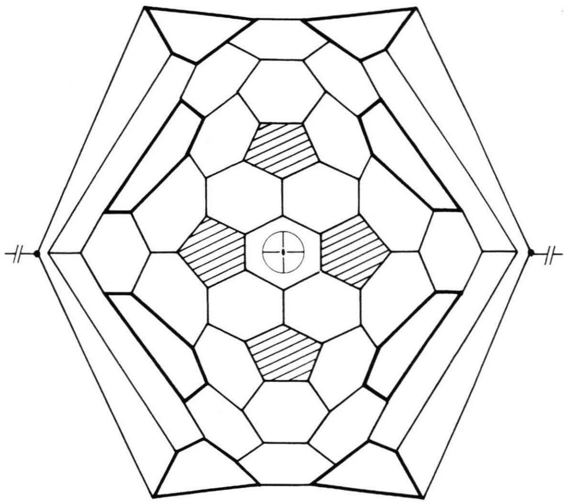

Fig. 1. Schlegel diagram of the C_{2v} topoisomer of C_{82}. Two types of pentagons have been discriminated in the schematic display. Eight pentagons, which are coupled to six pyracylene units, have been labeled by bold lines. Four pentagons, which are not coupled to such pyracylene units, have been symbolized by hatched areas. They are grouped around the C_{82} hexagon of site symmetry C_2 (central part of the corresponding Schlegel diagram).

2. Computational Conditions

We have used the GAUSSIAN 94 package [15] to evaluate the *ab initio* HF results of the next section. The basis set used in the geometry optimizations is of the STO 3G type. The final computational step leading to the data of section 3 is of 3-21 G* quality. In short, we have used the geometries optimized via the STO 3G basis for the subsequent 3-21 G* calculations. The spin state of Sc@C_{82} and the Sc atom is doublet. To determine the energies of these open shell systems we have employed the unrestricted variant of the *ab initio* HF (= UHF) approach. For the optimization of the different geometries, we have adopted the strategy described in our recent investigation of Sc@C_{82} [10]. We wish to point out that we have neglected the so-called basis set superposition error (BSSE) in the evaluation of the binding energy of the endohedral complexes.

3. Results and Discussion

In order to simplify the discussion of the computational results and the comparison with our previous 3(C_2) data [8 - 10] we have portrayed the Schlegel diagram of the C_{2v} topoisomer of the C_{82} cage in Figure 1. In comparison to the 3(C_2) geometry a new pentagon short-range order occurs under C_{2v} conditions. In the 3(C_2) topoisomer of C_{82} all pentagons are part of pyracylene units, molecular fragments which are formed by two pentagons and two hexagons. The coupling of the two pentagons occurs via a central 6-6 bond. In the C_{2v} cage, four pentagons occur which are not coupled to such pyracylene units. The remaining eight pentagons of the C_{2v} fullerene contribute to six pyracylene fragments. Figure 1 shows that the four uncoupled pentagons are grouped around a unique hexagon with site symmetry C_2, i. e., the corresponding hexagon contains the two-fold axis. Note that the C_2 axis cuts the center of the "central" hexagon in Figure 1. We want to emphasize that "decoupled" pentagon fragments as encountered in Fig. 1 are absent in the 3(C_2) topoisomer of C_{82}. As will be shown below, this new structural element is of high significance for the Sc coordination in the C_{2v} cage of Sc@C_{82}.

Table 1. Relative energies of the 3(C_2) and C_{2v} topoisomers of C_{82} (first column) and endohedral Sc@C_{82} emerging from the two C_{82} cages (second column). The energy minimum for both species has been set equal to zero. In the last column we have given the binding energy of the endohedral complexes. The computational results refer to *ab initio* HF calculations in a 3-21 G* basis. All numbers are given in eV.

C_{82} Topo-isomer	Energy	Sc@C_{82} Symmetry	Energy	Binding energy
3(C_2)	0.00	C_2	0.84	0.87
C_{2v}	1.93	C_{2v}	0.00	3.64
		C_s	0.06	3.58
		C_1	0.05	3.59

In Table 1 we have summarized the *ab initio* results of Sc@C_{82} emerging from the 3(C_2) and C_{2v} topoisomers of the bare fullerene molecule. The C_{2v} symmetry of C_{82} is conserved at the energy minimum of Sc@C_{82}. According to the present quantum chemical calculations, Sc is located on the two-fold axis above the hexagon with site symmetry C_2. In Fig. 2 we have given a schematic representation of Sc positions under C_{2v} symmetry of the endohedral complex (structure of lowest energy) and for the C_{2v} subgroups C_s and C_1. The C_s and C_1 configurations with spatially displaced Sc are only slightly higher in energy than the C_{2v} arrangement. In the point group C_s, Sc is located above the 6-5 bond C(α)-C(α) (see Fig. 2 for the definition of the C atoms). In the absence of any spatial symmetry (i. e. point group C_1), a manifold of quasi-degenerate

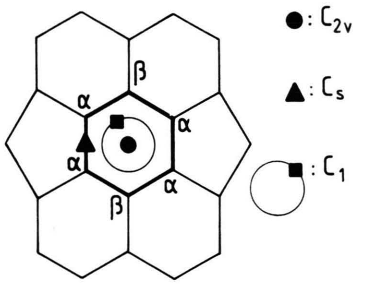

Fig. 2. Central subunit of the Schlegel diagram of Fig. 1: Schematic representation of the Sc positions encountered in the point groups C_{2v} (full circle), C_s (full triangle) and C_1 (full square) of Sc@C_{82} formed by a fullerene cage of C_{2v} symmetry. In the point group C_1, the Sc atom is located on an "inner ring" above the hexagon with site symmetry C_{2v}. The C_2 symmetry of the fullerene hexagon leads to two sets of inequivalent carbon atoms (C(α), C(β)).

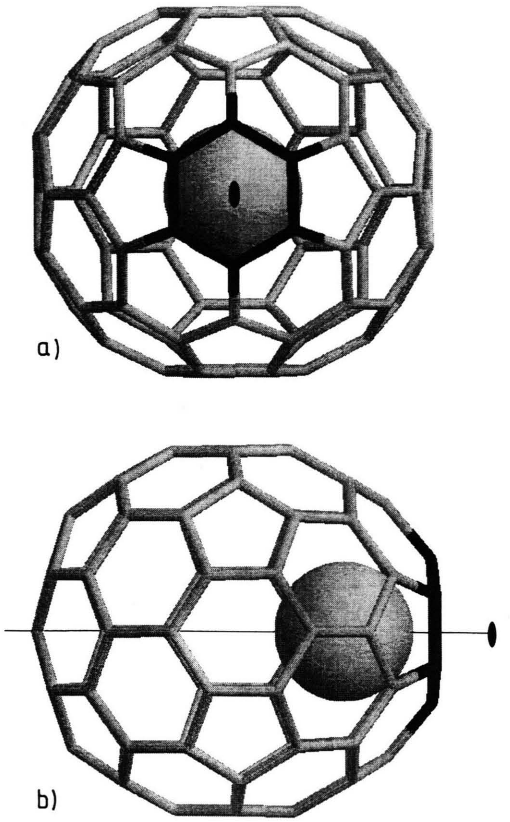

Fig. 3. Three-dimensional representations of the Sc@C_{82} minimum structure according to STO 3G calculations. a) shows a projection onto the plane of the coordinated hexagon. Note that the center of this 3D diagram corresponds to the center of Figure 1. b) corresponds to a projection observed after a 90° rotation of diagram a). The orientation of the C_2 axis has been emphasized in both diagrams.

Sc positions occurs. In the C_1 complex Sc is displaced somewhat from the hexagon center, an arrangement leading to two short and two long Sc-C contacts. In the schematic representation of Fig. 2, we have indicated the off-center positions accessible for Sc in the C_{82} system via an "inner" circle confined to the hexagon with site symmetry C_2. According to the present 3-21 G* calculations the C_s and C_1 structures of Sc@C_{82} are predicted 0.06 and 0.05 eV above the C_{2v} minimum. Three-dimensional (3D) representations of the structure of minimum energy are given in Figure 3. With increasing separation of the Sc atom from the C_2 hexagon, the energy of the complex is raised strongly. This energetic destabilization is particularly large if Sc is placed into pocket regions of the C_{2v} topoisomer of the C_{82} cage. This is in contrast to predictions for the 3(C_2) cage, in which Sc coordination occurs in a pronounced pocket region. The *ab initio* data in Table 1 suggest that the endohedral Sc atom experiences only a flat potential in the vicinity of the C_2 hexagon. The spatial uncertainty of the endohedral atom seems to be rather large within the boundaries of the corresponding hexagon. Such a behavior has been suggested in a recent density functional study of Ca@C_{82} [7]. The intrafullerene potential acting on Sc in the C_{2v} topoisomer of the C_{82} cage differs noticeably from the potential under 3(C_2) conditions where Sc is trapped in a local minimum confined by a high-energy barrier. The calculated binding energy of the Sc@C_{82} complex formed by a C_{2v} cage is much larger than the binding energy derived for the 3(C_2) cage. For the latter complex the 3-21 G* approach yields a binding energy of roughly 0.84 eV [9, 10]. If Sc is encapsulated in a C_{2v} cage, the binding energy is larger than 3.55 eV; see Table 1. The computational results in the table indicate a change in the energetic ordering of the two C_{82} topoisomers when going from the bare fullerenes to the endohedral complexes. Such changes in the energetic ordering have been predicted also in the transition from the neutral to the di- and trianionic C_{82} cages [7, 16]. In the absence of the endohedral donor atom the C_{2v} topoisomer is 1.93 eV higher in energy than the 3(C_2) arrangement; see Table 1. The large binding energy accessible for the C_{2v} descendants of Sc@C_{82} (C_{2v}, C_s, C_1) causes an inversion of the energetic ordering of the fullerenes in the transition from the bare fullerenes to the endohedral complexes. Sc@C_{82} with the 3(C_2) cage is 0.84 eV above the C_{2v} minimum.

Let us next discuss the Sc-C distances calculated for the C_{2v} energy minimum. The C_2 site symmetry of the coordinated hexagon implies two sets of Sc-C distances, i.e. four contacts of the type Sc-C(α) and two contacts of the type Sc-C(β); see again Fig. 2 for the definition of the carbon atoms. The Sc-C(α) and the Sc-C(β) contacts amount to roughly 242.7 and 243.7 pm. We want to emphasize that the C_{82} topoisomer considered, the Sc-C coordination and the Sc-C bondlengths predicted by the HF STO 3G approach are in line with synchrotron X-ray data reported some weeks ago at the International Winterschool on Electronic Properties of Novel Materials [17]. In this very recent study it has been demonstrated unambiguously that Sc@C_{82} is of C_{2v} symmetry, i. e. Sc is located on the two-fold axis of a C_{82} cage of C_{2v} point symmetry. The coordination number of Sc is six. The measured mean Sc-C distance amounts to roughly 254 pm. In the STO 3G approach the Sc-C separation is underestimated by roughly 4.5 %. The Sc coordination causes a non-negligible enhancement in the length of the C-C bonds of the coordinated hexagon. The calculated C(α)-C(β) bondlength in the bare fullerene amounts to 142.3 pm, while 144.2 pm are predicted for the two C(α)-C(α) bonds. In Sc@C_{82} the corresponding C-C bonds are elongated to 147.2 and 146.9 pm. The Sc-caused enhancement in the length of C-C bonds in the 3(C_2) topoisomer is much larger than the elongation encountered for the C_{2v} complex. In one of our recent *ab initio* studies of Sc@C_{82} with a 3(C_2) cage [10] spatial relaxations of the carbons have been derived which lead to bondlength elongations up to 9 pm. These large spatial rearrangement processes in the 3(C_2) descendant seem to be a result of the much shorter Sc-C contacts. In analogy to [8 - 10], we predict an incomplete Sc to C_{82} charge transfer (CT). The Mulliken net charge at the endohedral Sc atom amounts to 2.18. This incomplete CT is in line with experimental observations on M@C_{82} fullerenes (M = Sc, La) [17, 18]. A photoelectron spectroscopic investigation of La@C_{82} has shown that roughly one third of the valence charge of the La donor is not transferred to the fullerene unit.

4. Conclusions

The results of the present *ab initio* HF investigation of Sc@C_{82} can be summarized as follows:

i) The energetic sequence of the bare C_{82} topoisomers differs from the energetic sequence established for the endohedral materials. Although we have analyzed only two C_{82} topoisomers by rather time-consuming quantum chemical calculations we believe that changes in the energetic ordering in the transition from the bare fullerene cage to the endohedral complex are not restricted to the 3(C_2) - C_{2v} pair of C_{82} and Sc@C_{82}. In this context, we refer to the density functional calculations of [12] where such changes have been studied.

ii) Possible inversions in the energetic sequence of the bare C_{82} topoisomers in the transition to endohedral complexes suggest that the metal atom is encapsulated in a carbon cluster in an early stage of the fullerene formation.

iii) The present *ab initio* results as well as our previous findings [8 - 10] demonstrate that the coordination pattern of the endohedral donor atom and the degree of spatial trapping depend on the symmetry of the fullerene cage, i.e. on the short-range order of the fullerene pentagons and hexagons. In Sc@C_{82} formed by the 3(C_2) topoisomer we have predicted a Sc coordination above a 6-6 bond of a pyracylene unit which is part of the pocket region of C_{82}. The C_{2v} cage favors Sc coordination above a hexagon with site symmetry C_2. Within this hexagon, Sc can occupy different spatial positions, which are roughly degenerate in energy. Under 3(C_2) conditions the endohedral atom is strongly trapped.

iv) *ab initio* calculations (in a 3-21 G* basis) support experimental information of an incomplete metal to fullerene CT.

It is tempting to speculate why the most abundant MEF might be the one of lowest total energy. If this can be verified by further experiments and calculations for the complete set of C_{82} topoisomers, this would indicate an efficient interconversion mechanism for the topoisomers during the early steps of MEF synthesis.

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