J. Am. Chem. Soc. **1995,** *117,* 4623−4627

Magnetic Properties of $C_{60}H_{36}$ Isomers

Michael Bühl,*,† Walter Thiel,† and Uwe Schneider‡

Contribution from the Organisch-Chemisches Institut, Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland, and the Institut für Physikalische und Theoretische Chemie, Universität Karlsruhe, D-76128 Karlsruhe, Germany

Received January 2, 1995®

Abstract: The computed [GIAO (Gauge Including Atomic Orbitals)-SCF/tzp(He),dz(C,H)//SCF/3-21G] endohedral helium NMR chemical shifts for various $He@C_{60}H_{36}$ isomers (in parentheses) are −10.8 (T), −7.4 (D_{3d}'), −6.1 (S_6), −3.4 (T_h), and −5.6 ppm (D_{3d}). Despite 12 unusually long CC bonds (1.646 Å at SCF/3-21G), the T form has the lowest energy of all isomers studied and is more stable than T_h by ca. 59 kcal/mol (SCF/3-21G level). The computed $\delta(^3He)$ values depend primarily on the numbers of benzene rings present. It is suggested that the ^3He labeling and NMR technique, assisted by the computational results presented, could provide new information concerning the nature of the products arising from Birch reduction and hydrogenation reactions of C_{60}.

Introduction

Even though $C_{60}H_{36}$ has been the first reported derivative of C_{60},[1] its structure is still unknown. Identified as the principal product of the Birch reduction of C_{60}, a T_h symmetric structure has been inferred for $C_{60}H_{36}$ (Figure 1). The proposed structure possesses only isolated double bonds, consistent with the fact that conjugated or aromatic double bonds are usually attacked during Birch reduction.[2] However, recent sophisticated mass spectrometric analyses suggest that the C_{60} Birch reduction product is actually a complex mixture of polyhydrofullerenes $C_{60}H_{18}$−$C_{60}H_{36}$ with $C_{60}H_{30}$ and $C_{60}H_{32}$ as the major components.[3]

Transfer hydrogenation of C_{60} with dihydroanthracene affords $C_{60}H_{18}$ or $C_{60}H_{36}$, depending on the reaction conditions.[4] No ESR-detectable radical anions can be generated from the reaction products, which has been taken as evidence for the presence of isolated double bonds. Broad signal groups are prominent in the ^1H NMR spectrum; the same has been found for the Birch reduction products, where the broad signal shapes have been attributed to "the presence of isomers of $C_{60}H_{36}$ and possibly [to] the presence of $C_{60}H_{18}$."[1]

Hydrogen-radical-induced hydrogenation of fullerite (a mix of crude C_{60} and C_{70}) at elevated temperatures and hydrogen pressures is also reported to produce $C_{60}H_{36}$.[5] In contrast to the aforementioned substances, this species is insoluble in almost all solvents. From comparisons of the reduced density function obtained by electron and X-ray diffraction with those calculated for various molecular models, a D_{3d} symmetric structure has been proposed (Figure 1).[6] The solid-state ^{13}C NMR spectrum[5] may be reconciled with such a structure, but an unequivocal assignment of at least four sp^3 and three sp^2 carbon signals to hydrogenated C_{60} and C_{70} species is not possible.

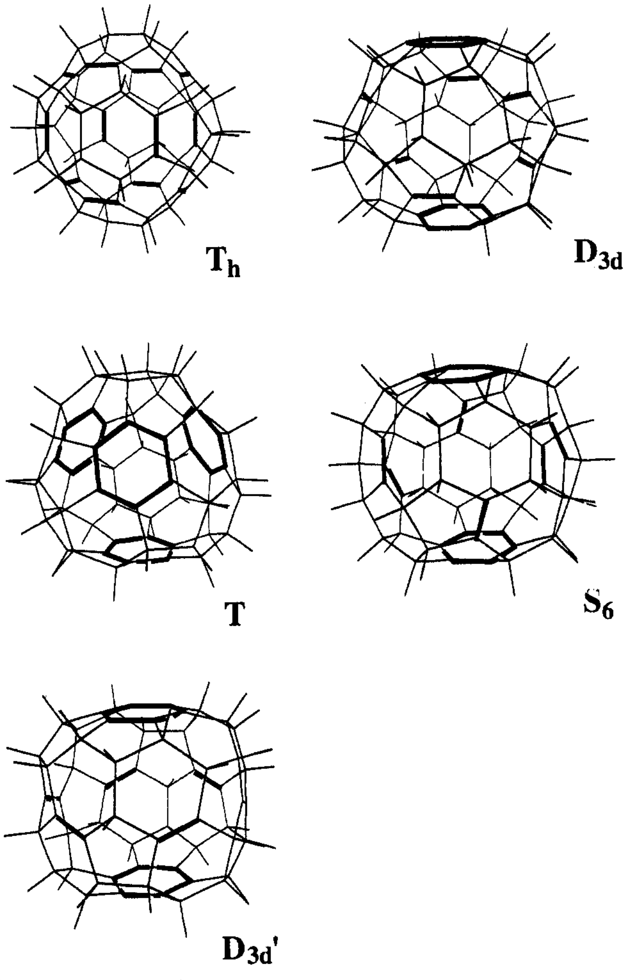

Figure 1. Schematic structures of the $C_{60}H_{36}$ isomers of this study Benzene rings and double bonds are indicated by bold lines.

Based on consideration of electronic (i.e. resonance) and strain energies, a chiral structure of T symmetry has been predicted as the most stable $C_{60}H_{36}$ isomer (Figure 1).[7] Factors favoring such a structure should be the aromaticity of the four retained

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† Universität Zürich.

‡ Universität Karlsruhe.

® Abstract published in *Advance ACS Abstracts,* April 1, 1995.

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benzene rings and the "geodesic" (i.e., even) distribution of strain. Recent semiempirical (MNDO, AM1, PM3),[8-10] ab initio, and density functional studies (DZ//STO-3G, BLYP/DZ//STO-3G)[11] found the T isomer lower in energy than the T_h form, with computed separations between ca. 16 (AM1)[10] and 97 kcal/mol (BLYP/DZ //STO-3G). Employing local density functional theory and geometries from an empirical potential, relative energies of ca. 0, 10, 48, and 54 kcal/mol have been given for the T, S_6 (Figure 1), T_h, and D_{3d} isomers, respectively.[12]

All ab initio results (including our own) agree that the T form of $C_{60}H_{36}$ is the most stable among the isomers considered so far. However, if the reactions believed to produce $C_{60}H_{36}$ are kinetically controlled, then the species that is formed is not necessarily the thermodynamically most favored one.[13] In order to assist in further spectroscopic studies, we now report ab initio calculated NMR chemcial shifts for the candidates discussed. Special attention is called to the endohedral NMR chemical shift at the very center of the cages.

Recently, ^{3}He NMR of endohedral fullerene compounds has been introduced as a sensitive probe for ring current effects,[14,15] and a wide ^{3}He chemical shift range (from ca. −6 to −28 ppm) has been observed for various ^{3}He labeled fullerenes and fullerene derivatives.[15] The analytical potential of this technique is that each endohedral compound is identified with a single, characteristic line in the ^{3}He NMR spectrum. In general, the signals are well-separated. Ab initio GIAO-SCF (Gauge Including Atomic Orbitals) chemical shift calculations reproduce the experimental ^{3}He chemical shifts of He@C_{60} and He@C_{70} with reasonable accuracy[16,17] and may be helpful in assigning corresponding peaks for higher fullerenes.[18] We now report GIAO-SCF computed endohedral chemical shifts for various He@$C_{60}H_{36}$ isomers. It is suggested that an experimental determination of this property might provide new information concerning the hydrogenation products of C_{60}. In particular, the endohedral helium shieldings for the two most discussed candidates, T and T_h, are predicted to differ by more than 7 ppm and should thus be readily distinguishable.

Computational Methods

Table 1. MNDO Heats of Formation (kcal/mol) and ab Initio Total (au) and Relative Energies (kcal/mol, in parentheses) of $C_{60}H_{36}$ Isomers

	MNDO		3-21G//3-21G		tzp(He),dz(C,H)// 3-21G[a] (E_{rel})
isomer	ΔH_f	(E_{rel})	E_{tot}	(E_{rel})	
T	229.0	(3.3)	−2280.30625	(0.0)	(0.0)
D_{3d}'	225.7	(0.0)	−2280.27137	(21.9)	(26.1)
S_6	229.1	(3.4)	−2280.25931	(29.5)	(33.0)
T_h	232.9	(7.2)	−2280.21291	(58.6)	(67.5)
D_{3d}	264.3	(38.6)	−2280.18218	(77.8)	(80.6)

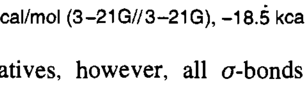
[a] Relative energies of He@$C_{60}H_{36}$ isomers, geometries of the pristine hydrofullerenes employed.

The geometries of the $C_{60}H_{36}$ isomers discussed hitherto in the literature (Figure 1) have been fully optimized with MNDO[19] in T_h, D_{3d}, T, and S_6 symmetry, respectively, followed by reoptimization at the SCF/3-21G level (denoted 3-21G in the following) employing the TURBOMOLE program.[20] In accord with recent semiempirical studies,[9,10] we found that another D_{3d} isomer (D_{3d}', Figure 1) is the most stable form at the MNDO level. The D_{3d}' geometry has also been refined at 3-21G. For both sets of geometries (MNDO and 3-21G), a helium atom has been placed in the center of mass (see below) and the NMR chemical shifts have been computed employing the direct version of the GIAO-SCF method[21] (as implemented in TURBOMOLE), together with the following contracted Huzinaga[22] basis sets: He tzp, (5s) [3s], augmented with one polarization function (α_p = 1.0); C dz, (8s4p) [4s2p]; H dz, (4s) [2s]. ^{3}He chemical shifts are reported relative to free He (σ = 59.9 ppm, tzp), δ(^{13}C) relative to TMS (σ = 200.8 ppm, dz basis, experimental geometry[23]). The common "energy (or chemical shift)//geometry" notation is used; e.g. "dz//3-21G" denotes an energy (or chemical shift) with a dz basis for a 3-21G optimized geometry.

Results and Discussion

Energies and Geometries. Absolute and relative energies of the $C_{60}H_{36}$ isomers are collected in Table 1. At the MNDO level, the energetic separations between the isomers are relatively small, and the D_{3d}' structure is the most stable form. With ab initio methods, the energetic discrimination between the isomers is larger. In particular, the T_h form is computed ca. 68 kcal/mol higher in energy than the T isomer [dz(C,H)//3-21G, Table 1], in agreement with the SCF/DZ//STO-3G value of 69.5 kcal/mol.[11] Electron correlation may increase this energy difference even more, since the reported BLYP/DZ//STO-3G value is 97.4 kcal/mol.[11] With all methods considered, the D_{3d} structure that has been deduced for the solid product of the high pressure hydrogenation[6] is higher in energy than the T_h form and is highly destabilized (up to ca. 81 kcal/mol) with respect to the structure of lowest energy, T.

The main factor that stabilizes other $C_{60}H_{36}$ isomers relative to the T_h form is the presence of aromatic benzene rings which the latter is lacking. The following isodesmic equation may serve as a quantitative estimate for this stabilization:



(1)

ΔE = −41.3 kcal/mol (3−21G//3−21G), −18.5 kcal/mol (MNDO)

In C_{60} derivatives, however, all σ-bonds are more or less eclipsed. If one employs the planar, eclipsed structures for cyclohexene (C_{2v} instead of C_2) and cyclohexane (D_{6h} instead of D_{3d}), the energy gain in eq 1 is reduced to −16.0 kcal/mol (3-21G//3-21G level, MNDO: −9.7 kcal/mol). Thus, relative

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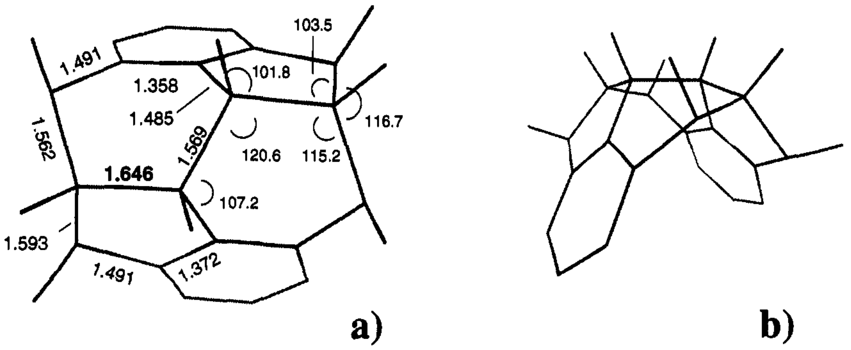

Figure 2. Section of the $C_{60}H_{36}$ *T* structure illustrating the geometry around the elongated CC bonds: (a) view along a 2-fold axis with selected 3-21G optimized bond lengths [Å] and angles [degrees] included; (b) side view.

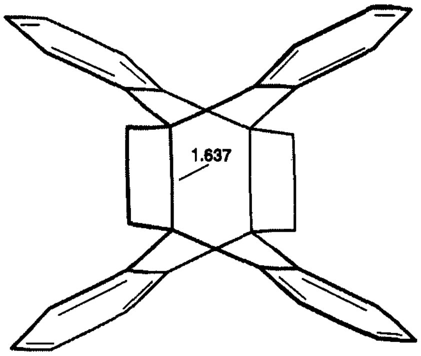

Figure 3. Schematic structure of the bi(anthracene-9,10-dimethylene) photoisomer. The elongation of the labeled CC bond (3-21G value from ref 24) is partly due to hyperconjugation.

Table 2. GIAO-SCF/tzp(He),dz(C,H) Computed NMR Chemical Shifts (in ppm) of $He@C_{60}H_{36}$ Isomers

		$\delta(^3He)^c$	
isomer	$\delta(^{13}C)^a$, //3-21G^b	//3-21G^b	//MNDO^d
T	25.7 (12), 37.1 (12), 43.8 (12), 132.5 (12),^{e} 136.5 (12)^e	−10.8	−10.3
D_{3d}'	27.4 (6), 30.0 (12), 32.1 (12), 37.2 (6), 125.6 (12), 135.1 (12)^e	−7.7	−7.4
S_6	30.3 (6), 33.7 (6), 34.2 (6), 36.2 (6), 37.6 (6), 39.2 (6), 127.8 (6), 134.9 (6), 142.7 (6),^{e} 142.8 (6)^e	−6.1	−6.3
T_h	27.6 (12), 39.7 (24), 129.6 (24)	−3.4	−3.5
D_{3d}	28.5 (6), 35.3 (6), 36.1 (12), 37.9 (12), 135.1 (12), 148.8 (12)^e	−5.6	−6.6
Expt^f	*31, 38, 44, 49, 128 (weak), 134, 138*		

^{a} Relative to TMS, intensities in parentheses. ^{b} 3-21G geometry employed. ^{c} Relative to free He. ^{d} MNDO geometry employed. ^{e} Benzene carbons. ^{f} Solid-state NMR of the high-pressure hydrogenation product of fullerite, ref 5.

energies of ca. 0, 32, and 64 kcal/mol would be expected for the $C_{60}H_{36}$ isomers with four, two, and zero benzene rings, respectively. These numbers agree surprisingly well with the ab initio energies for the *T*, D_{3d}'/S_6, and T_h isomers in Table 1. The D_{3d} form appears to suffer from additional strain, as it is at least 50 kcal/mol higher in energy than expected from the above considerations.

However, the most stable isomer, *T*, also exhibits signs of strain in the σ-framework, manifested in a rather long C−C bond, 1.646 Å (3-21G level, MNDO: 1.612 Å, see Figure 2). A similarly long CC distance has been computed for the bi(anthracene-9,10-dimethylene) photoisomer (1.637 Å at 3-21G, Figure 3).[24] The bond elongation in the latter has been partly attributed to hyperconjugation (i.e. $\pi \rightarrow \sigma^*$ or $\sigma \rightarrow \pi^*$ interactions) between the benzene π-system and the CC σ-bond which are oriented almost perpendicular (thus permitting effective overlap of the corresponding MOs). In the *T* isomer of $C_{60}H_{36}$, the elongated bond lies in the plane of the nearest benzene ring, precluding a similar σ/π hyperconjugation.

The long CC bond in the *T* form (there are actually 12 symmetry-equivalent bonds) is also apparent in the MM3[25] structure (1.641 Å). A constrained MM3 optimization with the critical bonds fixed to 1.5258 Å, i.e. the optimal MM3 r_0 value for this type of bond, increases the heat of formation by ca. 35 kcal/mol.[26] Analysis of the steric energy decomposition shows that the gain in total stretching energy due to this bond "compression" (ca. 30 kcal/mol) is balanced by an equivalent increase in total bending energy. Most of the destabilization of the constrained structure arises from an increase in the total torsional energy (ca. 20 kcal/mol), which appears to be distributed rather evenly among most of the ca. 600 dihedral angles and not concentrated in certain areas. Thus, the unusual CC bond lengthening in the T ground state may be due to relief in torsional strain in order to accommodate the four, almost planar benzene rings.

Carbon−carbon σ-bonds in C_{60} derivatives tend to be somewhat elongated compared to those in "normal" organic molecules. For example, a CC distance of 1.62(4) Å has been reported for a Diels−Alder adduct of C_{60},[27] and bond lengths of 1.585 and 1.614 Å are computed for [6,6]- and [5,6]-$C_{60}H_2$, respectively, at the 3-21G level. The longest, 3-21G computed CC distances in each of the other $C_{60}H_{36}$ isomers are 1.592 (T_h), 1.602 (S_6), 1.629 (D_{3d}'), and 1.580 Å (D_{3d}).

Chemical Shifts. The computed ^{13}C and ^3He NMR chemical shifts of the $C_{60}H_{36}$ isomers are summarized in Table 2. It should be noted that the basis set on C and H is probably too small for quantitative predictions of ^{13}C chemical shifts. For example, it has been shown that large basis sets of TZP quality are needed for a good description of the $\delta(^{13}C)$ values in C_{70} (although the ordering of two close-lying signals is reversed even at that level).[21] At the dz//3-21G level, a ^{13}C chemical shift of 150.7 ppm is computed for C_{60}, i.e. deviating by 8 ppm from the experimental value (142.7 ppm).[28]

For the products of the high-pressure hydrogenation of fullerite, a solid-state ^{13}C NMR spectrum has been reported with

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at least 4 and 3 signals in the sp^3 and sp^2 regions, respectively[5] (see Table 2 for the numbers). Keeping in mind the uncertainties of the experimental and theoretical data, it appears that isomer T fits the experimental spectrum somewhat better than the proposed D_{3d} structure: The separation of the two sp^2 signals computed for T, ca. 4 ppm, matches the experimental difference between the two largest peaks in that region (4 ppm) while the separation computed for D_{3d} is much larger, ca. 13 ppm (Table 2). It is also interesting to note that the T isomer is the only one with a computed sp^3 $\delta(^{13}C)$ value larger than 40 ppm (calculated ca. 44 ppm), approaching the most deshielded experimental value in that region, 49 ppm.

As pointed out above, interpretation and assignments of ^1H and ^{13}C NMR spectra may be hampered by the presence of various, possibly isomeric hydrofullerenes. ^3He NMR spectroscopy of the corresponding endohedral helium compounds would constitute a potentially "cleaner" analytic tool since only one signal is expected for each species and isomer. The computed endohedral ^3He NMR chemical shifts in Table 2 range from $\delta = -3.4$ (T_h) to -10.8 ppm (T), i.e. from 2.9 ppm downfield to 4.5 ppm upfield with respect to the experimental value of He@C_{60}, -6.3 ppm. So far, derivatization of He@C_{60} has exclusively resulted in increased shielding (i.e. additional upfield shifts) of the endohedral helium atom, cf. $\delta = -9.4$ for the pyrrolidine mono-adduct and $\delta = -10.9$ and -12.3 ppm for two bis-adducts.[15a] The $\delta(^3He)$ value predicted for the T form of $C_{60}H_{36}$, -10.8 ppm, lies in the same range, so that an unequivocal identification of this isomer might be difficult if lesser hydrogenated species are present. However, if the T_h form were the major hydrogenation product, its $\delta(^3He)$ signal should be readily distinguishable downfield from He@C_{60}, i.e. in an area not usually covered by C_{60} derivatives. Hence, we would expect that ^3He NMR of a hydrogenated He@C_{60} sample will furnish strong evidence for or against the presence of the T_h isomer of $C_{60}H_{36}$.

The computed ^3He chemical shift in He@C_{60} proved to be particularly sensitive to the geometry employed for the fullerene cage.[17] In the fullerenes, the endohedral chemical shifts arise from both diamagnetic and paramagnetic ring currents in the six-membered and five-membered rings, respectively.[29] The paramagnetic contributions to the nuclear shielding are often quite sensitive to geometrical changes, which may account qualitatively for the pronounced dependence of the theoretical $\delta(^3He)$ value with the structural parameters in He@C_{60}.[17] In the He@$C_{60}H_{36}$ isomers of this study, only "classical", i.e. diamagnetic, currents in benzene rings are present. Therefore, we would expect a much smaller geometry dependence of $\delta(^3He)$ than found for He@C_{60}. Indeed, going from the 3-21G to the MNDO geometries affects the computed ^3He chemical shifts of the He@$C_{60}H_{36}$ isomers only marginally (a few tenths of a ppm, except for D_{3d}, cf. Table 2).

As expected, the computed endohedral shielding increases with the number of benzene rings present. The lowest shielding is found for the T_h form (no benzene rings), the largest for the T isomer (4 benzene rings), and intermediate values for the other isomers (2 benzene rings each). The ring-current-induced chemical shifts in and above the molecular plane of benzene have been the subject of numerous theoretical studies[30] (mainly employing Hückel MO-based London calculations), and extensive amounts of data have been tabulated.[31] What chemical shift would a noninteracting nucleus like He be experiencing at a given distance above a single benzene molecule? As a rough estimate, we computed the chemical shifts of various points in space along the symmetry axis of benzene at the dz//3-21G level (Table 3).[32] The same calculation has been carried out for ethylene (perpendicular to the molecular plane), in order to estimate the anisotropy effect of an isolated double bond. As found for the ring-current effect above benzene, the anisotropy effects above ethylene are shielding, albeit one order of magnitude smaller than the former. Table 4 lists the distances of the central helium atoms to the midpoints of the benzene and ethylene moieties in each of the $C_{60}H_{36}$ isomers. Assuming additivity of the ring-current and anisotropy effects, one can arrive at very simple estimates for the endohedral chemical shifts by interpolating[33] the numbers in Table 3 according to the actual distances and summing over all benzene and ethylene units present.[34] The agreement of the chemical shifts estimated in such a way with the actual, computed $\delta(^3He)$ values is remarkable (Table 4). Evidently, the endohedral chemical shifts

Table 3. Variation of the Computed Chemical Shifts[a] with the Distance Perpendicular to the Molecular Planes (in Å) of a Single Benzene and Ethylene Molecule, dz//3-21G Level

distance	benzene	ethylene
4.5	−0.69	−0.07
4.0	−0.97	−0.10
3.5	−1.39	−0.14
3.0	−2.11	−0.20
2.5	−3.36	−0.39
2.0	−5.58	−1.28

[a] Negative absolute shieldings in ppm of a point in space (isotropic values).

Table 4. Geometrical Parameters and Endohedral Chemical Shifts of $C_{60}H_{36}$ Isomers

isomer	distance[a] from benzene	distance[a] from ethylene	chemical shift estimated[b]	$\delta(^3He)$[c] calcd
T	2.82		−10.2	−10.8
D_{3d}'	2.83	3.35	−6.0	−7.7
S_6	3.05	3.23	−5.2	−6.1
T_h		3.33	−2.0	−3.4
D_{3d}	3.17	3.18	−4.9	−5.6

[a] Distances in Å from the center to the midpoint of the benzene and ethylene moieties in the 3-21G geometries of the $C_{60}H_{36}$ isomers. [b] Chemical shift of a central atom, estimated by interpolating the data in Table 3 to the actual distances and summing up the contributions of all benzene and ethylene units. [c] tzp(He),dz(C,H)//3-21G values from Table 2.

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(32) The ab initio numbers in Table 3 are larger (i.e. more strongly shielded) than the London values given in refs 30 and 31, probably because not only π-electron ring current effects are included but also the anisotropy effects of the CC and CH σ-bonds.

(33) The interpolation was done using the following fitting functions: $\sigma = 0.21 + 39.22e^{-x}$ (benzene) and $0.01 + 4.41e^{-x}$ (ethylene), where x is the distance (in Å) above the benzene and ethylene planes, respectively.

(34) For a direct use of the data in Table 3, the line connecting the He atoms with the midpoints of the benzene and ethylene moieties in the He@$C_{60}H_{36}$ isomers should be normal to the benzene and ethylene planes, respectively. While this holds for the positions with respect to the benzene moieties (the He atoms lie on 3-fold axes passing through the benzene midpoints) this is not exactly true for the ethylene units. However, the additional changes in the estimated chemical shifts due to these displacements from the "ideally perpendicular" positions should be very small.

in the He@$C_{60}H_{36}$ isomers can be accounted for by ring-current and anisotropy effects of the benzene and the ethylene moieties.

To what extent do the computed $\delta(^3He)$ values depend on the mobility of the endohedral helium atom? In the case of the fullerenes, the magnetic field inside the cages appears to be very homogenous.[29] Accordingly, when the helium atoms are displaced out of the central positions in He@C_{60} and He@C_{70} by as much as 1 Å, the computed endohedral chemical shifts are not affected notably (ca. 0.1−0.3 ppm).[17] As the helium atom moves away from the center it approaches certain current flows while it increases the distances to others, resulting in a small net change of the ring-current induced chemical shift. The same should hold for most of the He@$C_{60}H_{36}$ isomers of this study, except for the *T* form: When the helium atom moves away from one benzene ring[35] on a 3-fold axis, it shifts more or less parallel with respect to the other three. Since the ring-current-induced chemical shift is expected to vary much stronger perpendicular to the benzene plane than parallel to it,[30,31] such a displacement along a C_3 axis might have a net effect on $\delta(^3He)$. Indeed, a point in space on a C_3 axis 1 Å away from the center (opposite from a benzene ring) is less shielded (calculated $\sigma = 9.9$ ppm) than the central point ($\sigma = 10.8$ ppm, dz//3-21G level). Points on the C_2 axes ±1 Å away from the center ($\sigma = 10.6$ ppm) experience almost the same shielding as the center itself. Therefore, a slight downfield shift from the computed $\delta(^3He)$ values in Table 2 due to the He mobility might be expected for the *T* form, but probably less than 1 ppm. The conclusions regarding the differentiation of the T_h form from the other isomers should not be affected by this argument.

Conclusion

Ab initio 3-21G//3-21G energy calculations indicate that the chiral *T* form is the most stable structure among several $C_{60}H_{36}$ isomers considered. In particular, it is considerably lower in energy than the T_h isomer, in accord with previous ab initio and density functional studies.[11,12] The *T* isomer is energetically most favorable because it comprises the maximum number of aromatic benzene rings possible in this set of structures. In order to accommodate four planar benzene rings, however, considerable steric strain is built up in the σ-framework, as is evident from 12 (symmetry-equivalent) unusually long CC distances of 1.646 Å (3-21G level). Hence, this isomer may be among the organic molecules with the longest CC bonds known to date.

The computed [GIAO-SCF/tzp(He),dz(C,H)//3-21G] endohedral ^3He NMR chemical shifts of the He@$C_{60}H_{36}$ isomers can be related semiquantitatively to the ring-current and anisotropy effects of the benzene and ethylene moieties present; the shielding of the central helium atom increases with the number of benzene rings. As a consequence, the theoretical $\delta(^3He)$ values for the *T* and the T_h forms differ by more than 7 ppm. Since the latter has been suggested as the major product in Birch reduction or hydrogenation reactions of C_{60}, we propose that ^3He NMR spectroscopy could provide new information regarding the nature of the (correspondingly labeled) reaction products. In particular, if the proposed T_h form were present in significant amounts, it should be easily identified by its ^3He signal downfield from He@C_{60}.

Acknowledgment. This work was supported by the Alfried-Krupp-Stiftung. M.B. gratefully acknowledges a fellowship by the Fonds der Chemischen Industrie. Calculations have been performed on IBM RS/6000 workstations of the Institut für Organische Chemie and at the "C4 cluster" of the ETH Zürich. We thank Dr. D. Bakowies for assistance with his adapted version of the MM3 program.

JA950002X

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(35) Due to the flattening of the cage structure around the benzene rings, the center in the *T* form is closer to these (2.82 Å) than to the opposite, saturated six-membered rings (3.62 Å). Thus, displacement away from the benzene moieties might be expected.