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Aza-Dihydro[60]fullerene in the Gas Phase. A Mass-Spectrometric and Quantumchemical Study.

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Key words: *[60]fullerene, 1,2-azirino-[60]fullerene, aza-heterofullerene, AM1 and AMBER calculations*

Abstract: *A new approach to produce heterofullerenes is described. Starting from a fullerene with an intact cage which is activated by suitable exohedral functionalization, the first aza-heterofullerene is generated in the gas phase under DCI mass-spectrometric conditions. On the basis of AM1-calculations the 1,2-closed structure is proposed to be the most stable one.*

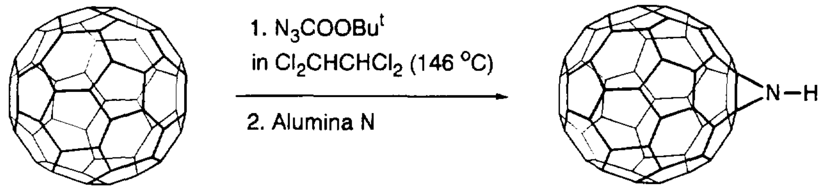
INTRODUCTION

Ever since fullerenes were discovered in 1985 by Kroto et al.[1] and ever since they were produced in macroscopic quantities in 1990 by Krätschmer and Huffman[2], heterofullerenes have attracted considerable interest.[3-6] So far only fullerenes containing boron such as $C_{59}B$, $C_{58}B_2$ and $C_{69}B$ have been generated by laser vaporization of a boron/graphite composite target rod at 1200 °C[3] or by arc evaporation of graphite rods doped with boron nitride.[6] Another attractive heteroatom is nitrogen and already in 1991 Karfunkel et al.[5] presented some evidence that hypothetical heterofullerenes of the type $C_{58}N_2$ might be stable on the basis of semiempirical calculations. Other theoretical approaches were reported by Kurita et al.[7] and recently Wang et al.[8] In 1991 Rao and coworkers already investigated the contact-arc vaporization of graphite in a partial atmosphere of N_2 or NH_3 which gave some evidence for the generation of nitrogen-doped fullerenes.[9]

We now wish to report our studies regarding the aza[60]fullerene system. Our results may open an alternative access to heterofullerenes starting from the intact fullerene cage which is activated by a suitable exohedral functionalization.

RESULTS AND DISCUSSION

The activated [60]fulleroid we chose was 1,2-(2,3-dihydro-1*H*-azirino-[60]fullerene which can be synthesized easily from C_{60} and tert-butylazidoformate in 40% yield overall (Scheme 1).[10]



1 **2**

Scheme 1. Synthesis of 1,2-(dihydro-1*H*-azirino)-[60]fullerene 2

Mass-Spectrometric Studies

The DCI (desorptive chemical ionization) mass spectrum (Fig. 1a) of **2** ($C_{60}NH$) with ammonia as reagent gas and a rhenium wire as heater shows besides the weak $[M+H]^+$ and the $C_{60}^{+\bullet}$ and $C_{60}H^+$ peak additional signals at m/z 723 and 724. With iso-butane as reagent gas, the peaks at m/z 723/724 are not enhanced (Fig. 1b). This cluster can be totally explained by a superposition of the calculated isotope patterns of $C_{60}^{+\bullet}$ and $C_{60}H^+$.

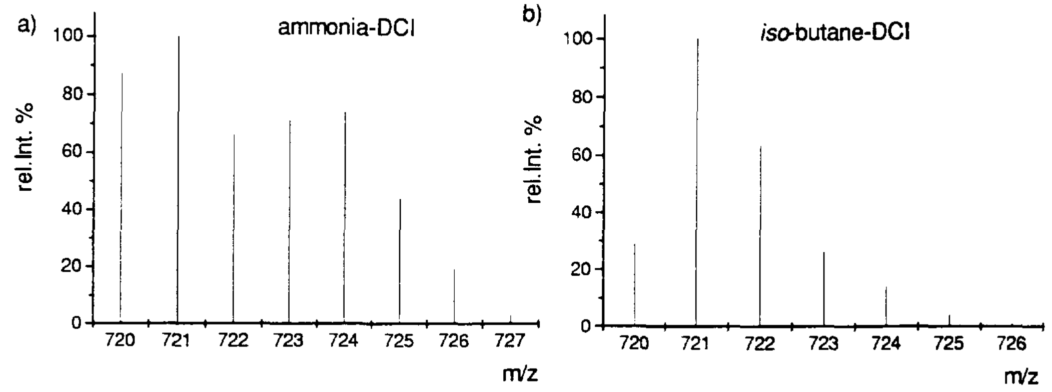


Fig. 1. Partial spectrum of 1,2-(dihydro-1*H*-azirino)-[60]fullerene **2** a) NH_3 DCI, b) *iso*-butane-DCI

On the contrary, the additional peaks at m/z 723 and at 724 which are formed under NH_3-DCI conditions can be best rationalized as $C_{59}NH^{+\bullet}$ and $C_{59}NH_2^+$. With this assumption the analysis of the cluster gives the relative amounts of the ions to be approximately $C_{60}^{+\bullet}/[C_{60}+H]^+/C_{59}NH^{+\bullet}/C_{59}NH_2^+ = 9/4/6/4$.

In order to confirm the elemental composition, the exact masses of the peaks are determined. Especially the most interesting ions at m/z 723 and at 724 contain contributions from the isotope peaks of the lighter species. The exact masses are shown in Table 1. The very small mass difference between peaks of equal nominal mass makes it impossible to separate them by increasing the resolution (it would be necessary to have a resolution in excess of 150000 m/Δm). Nevertheless it is possible to calculate the centroid mass of these composed peaks. These fit very well the experimentally found mass values.

Table 1. Calculated/Found Mass Values

Nominal mass	720	721	722	723	724*	725
Formula	$^{12}C_{60}$	$^{12}C_{59}{}^{13}C$	$^{12}C_{58}{}^{13}C_2$	$^{12}C_{57}{}^{13}C_3$		
Mass	720.0000	721.0034	722.0067	723.0101		
Formula		$^{12}C_{60}H$	$^{12}C_{59}{}^{13}CH$	$^{12}C_{58}{}^{13}C_2H$	$^{12}C_{57}{}^{13}C_3H$	
Mass		721.00783	722.01118	723.01454	724.01789	
Formula				$^{12}C_{59}NH$	$^{12}C_{58}{}^{13}CNH$	$^{12}C_{57}{}^{13}C_2NH$
Mass				723.01089	724.01422	725.01754
Formula					$^{12}C_{59}NH_2$	$^{12}C_{58}{}^{13}CNH_2$
Mass					724.01872*	725.02205
Mean (weighted)	720.00000	721.005137	722.009281	723.011299	724.016517	725.02058
Found		721.0016	722.0086	723.0121	724.0140	725.0195
Deviation [mmu]		3.5	0.7	-0.8	2.5	1.0

* The exact mass of m/z 724 is independently controlled with a more precise mass spectrometer and matched to the expected value better than 0.1 mmu (cf. Experimental).

Alternatively the m/z 724 could be explained as $C_{58}N_2^{+\bullet}$ or $C_{59}O^{+\bullet}$, but the difference of the determined to the calculated masses (7.2 and 19 mmu) are beyond the expected mass error of 5 mmu. The amount of the $C_{59}NH$ $^{+\bullet}$ and $C_{59}NH_2^+$ depends on the experimental conditions and it is obvious, that these ions are formed by a reaction with the reagent gas and / or the NH_4^+ ions. Fig. 1a) shows an example where these componds are formed in mean yield.

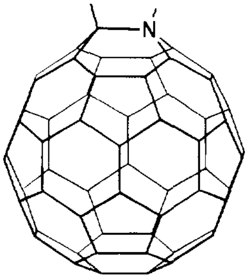
Table 2: Relative energies for the geometries obtained with AM1 and AMBER.

Compound	Connect.	AM1 ΔH_f a)	Dipole b)	Few most intense vib. c)	AMBER energy d)
1: C_{60}	-	973.3	0.0002		998.7
3: $C_{59}NH_2^+$	1,2	1136.7	9.02	1318. 1416. 2958. 3178	
4: $C_{59}NH_2^+$	1,6	1153.3	8.72	1028. 1544. 1722. 2967. 3192	
5: $C_{59}NH$	1,2	962.5	0.94	1103. 1523. 1836. 2995	939.5
6: $C_{59}NH$	1,6	978.9	1.00	1105. 1185. 1575. 1727. 1801. 1841. 3004	935.6
7: $C_{60}H_2$	1,2	931.2	2.87	1177. 1273. 1801. 3014. 3027	934.9
8: $C_{60}H_2$	1,6	950.0	2.60	1085. 1183. 1538. 1583. 1835. 3024. 3035	932.2
9: $C_{58}N_2$ [5]	1,2	1016.5	1.9		891.1
10: $C_{58}N_2$ [5]	1,6	1030.9	2.1		896.2

a) Heats of formation in kcal/mol; b) Dipole moment in Debye,
c) Vibrational frequencies in cm^{-1}, d) Energies in kcal/mol

AM1 and Force Field Calculations

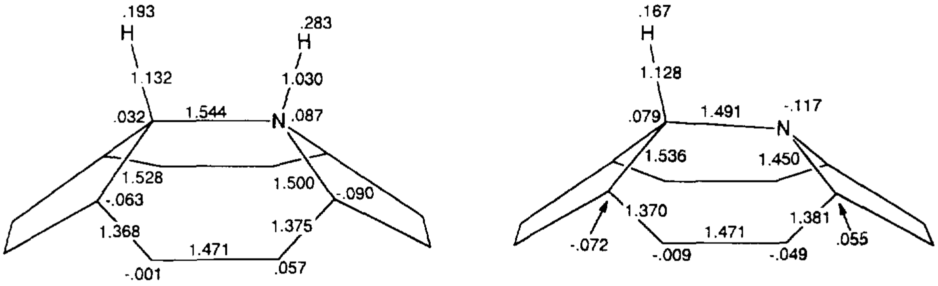
In order to elucidate the structure of the cluster, we performed both AM1[11] and AMBER[12] calculations. For better comparisons we did not focus solely on the charged species $C_{59}NH2^+$ but also on $C_{59}NH$. The latter is isoelectronic to $C_{60}H2$ which was calculated as well. In each case we considered the substitution pattern of the sp^3-hybridized centers at 1,2 connection and 1,6-connection. Please note that we do not want to present and discuss certain observables. Our aim is rather to make comparisons and to draw conclusions within a set of consistent series.



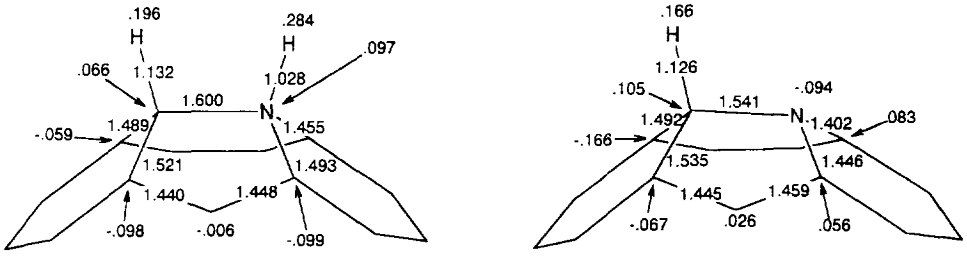
3 $C_{60}NH_2^+$ (1,2)

The geometries were constructed and fully optimized with the AMBER force field as implemented in MOBY.[13] Subsequently, MOPAC 7.0[14] is used to optimize the geometries with AM1. Table 2 summarizes the results of the different calculation methods.

For the semiempirical calculations the striking difference between the 1,2 isomers (C_{2v}-symmetry) and the 1,6 isomers of 15-18 kcal/mol indicates the stability of the former geometries.[15] Only the heterofullerene **5** reveals a greater stability than C_{60}[16] which is regarded as reference (bond lengths: 1.464Å for 1,6 and 1.385Å for 1,2 connected centers). In Fig. 2 only the upper rim of the compounds are shown. Only these centers reveal deviations from the reference lengths in the vicinity of the sp^3-hybridized centers and possess a remarkable charge separation.



3 $C_{59}NH_2^+$ (1,2) **5** $C_{59}NH$ (1,2)



4 $C_{59}NH_2^+$ (1,6) **6** $C_{59}NH$ (1,6)

Fig. 2. Calculated geometries and charges of **3**, **4**, **5** and **6**.

Considering the bond lengths between the sp^3-hybridized centers, the 1,2-isomers are significantly shorter by 5 pm (**3**/**4**) and 5.6 ppm (**5**/**6**). AM1 is known for overemphasizing the charge distribution of C-H and N-H bonds and therefore the observed charge of 0.283 for the hydrogen at **3** is due to this reason. Although nitrogen possesses a greater electronegativity; the charge at **6** is smaller than at the C-H carbon. Furthermore the charge's sign alternates at the following atoms which is typical for this substitution pattern. The isoelectronic 7 and **8** ($C_{60}H_2$) are 29-32 kcal/mol more stable than **5** and **6**.

The angle sum at the C-H carbon (**3**: 327°, **6**: 329°) clearly indicates the sp^3-hybridization because a sp^2-hybridization gives an angle sum of 3 x 120° = 360°. Therefore, the increase in stability can mainly be attributed to the introduction of sp^3-hybridized centers. This observation is in accord with the results of Karfunkel and Haddon.[5,17] Ongoing to the results determined by the force field, the stabilities are inverted. Now, the 1,6 isomers are 2.5-4 kcal/mol more stable and, in addition, have gained about 60 kcal/mol compared to C_{60} resembling $C_{60}H_2$.[18]

We were not able to reproduce the findings of Karfunkel whose AMBER energies were lower than in our case. Nevertheless, we consider the semiempirical calculations to be more substantial. Since this method proved to give reliable results[19] and accounts for the perturbation of the π-conjugation, it gives a better insight into the relative stabilities than a force field.

Summarizing the quantumchemical calculations, the introduction of the sp^3-hybridized centers results in a geometry which locally reduces the curvature. Overall we presented arguments that the observed mass spectra peaks can be assigned the 1,2 connected molecule $C_{59}NH_2^+$. Experiments to elucidate the process of formation are in progress.

CONCLUSION

On the basis of the mass spectrometric studies we have presented evidence for the formation of aza-dihydro-[60]fullerene in the gas phase. Basing on quantumchemical calculations we propose a 1,2-closed structure as the most stable for both the neutral ($C_{59}NH$) and the charged species ($C_{59}NH_2^+$). At this stage we can only speculate about the reaction starting from the exohedral functionalized fullerene **2.** Since $C_{59}NH/C_{59}NH_2^+$ is only generated with ammonia as reagent gas we assume firstly a reaction of **2** with NH_3/NH_4^+ and secondly a fragmentation under loss of a CN unit and hydrogens. This corresponds to observations by Smalley et al.[20] that fragmentation of fullerenes normally occurs by loss of C_2 units, down to C_{32}[19]. Our results can be taken as a new approach for the generation of $C_{59}NH/C_{59}NH_2^+$ or even other heterofullerenes at a laboratory scale.

EXPERIMENTAL

1,2-(Dihydro-1H-azirino)-[60]fullerene **2** was synthesized as described earlier.[10]

The mass spectrometer was a Finnigan-MAT 8230 double focussing magnetic sector field instrument equipped with a combined EI/CI ion source and SS300 data system. The reagent gas pressure was $3{,}5 \cdot 10^{-1}$ mbar and the source temperature 240°C, the resolution was adjusted to 3000 m/Δm.

The $C_{60}NH$ (**2**) was deposited as solution in toluene on the rhenium wire of the DCI-inlet system evaporated to dryness and introduced. The wire-current was increased within 60 sec to approximately 700°C. During this time the magnet was set to mass 715 and the accelerating voltage was cyclic downscanned over the desired mass range. The ion m/z 720.000 was chosen as lockmass to compensate for the scanjitter. The control measurement of m/z 724 was taken under comparable CI-conditions at Finnigan-MAT (Bremen) with a MAT 95F and automatic peakmatch procedure (R = 5000 m/Δm).

The geometries of the proposed heterofullerenes were constructed and fully optimized with the AMBER force field as implemented in MOBY.[13] Subsequently, MOPAC 7.0[14] is used to optimize the geometries with AM1 until the gradient norm drops below 0.1 kcal/mol*Å. By using Cartesian coordinates[5] the calculations were completed within an hour on an IBM-RS6000-32H workstation (MOPAC key words XYZ, GNORM=0.1, and PRECISE are sufficient). In order to check the results, calculations of the Hessian proved the existence of minimum geometries by showing only positive eigenvalues.

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