Mechanism of the Addition Reaction of Alkyl Azides to [60]Fullerene and the Subsequent N_2 Extrusion to Form Monoimino-[60]fullerenes

Montserrat Cases,[†] Miquel Duran,[†] Jordi Mestres,[‡] Nazario Martín,[§] and Miquel Solà[†,*]

Institut de Química Computacional, Universitat de Girona, E-17071 Girona, Catalonia, Spain,
Computational Medicinal Chemistry, Organon Laboratories Limited, Newhouse,
Lanarkshire ML1 5SH, Scotland, and Departamento de Química Orgánica, Facultad de Química,
Universidad Complutense, E-28040 Madrid, Spain

miquel.sola@udg.es

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The 1,3-dipolar cycloaddition of methyl azide to C_{60} and the subsequent nitrogen elimination from the formed triazoline intermediate to yield the aziridine adduct have been studied using semiempirical and density functional methods. The results obtained show that the addition of methyl azide to C_{60} takes place in the ring junction between two six-membered rings leading to a closed [6,6]-triazoline intermediate with an energy barrier of about 20 kcal mol^{-1} and an exothermicity of ca. 2 kcal mol^{-1} at the B3LYP/6-31G**//AM1 level of theory. The subsequent thermal loss of N_2 takes place through a stepwise mechanism in which the cleavage of the N−N single bond precedes the breaking of the N−C bond, with a total activation energy of approximately 45 kcal mol^{-1}. The N_2 loss occurs simultaneously with the formation of the new N−C bond. During the process, the steric effects of the leaving N_2 molecule prevent the addition of the nitrene substituent to the [6,6]-ring junction attacked initially and force the addition to an adjacent [5,6]-ring junction.

Introduction

Imino derivatives of fullerenes[1,2] have recently attracted considerable interest for two main reasons. First, iminofullerenes are the precursor compounds in the synthesis of nitrogen heterofullerenes.[3] Heterofullerenes[4] are modified fullerenes in which one or more carbon atoms have been substituted by heteroatoms, such as nitrogen or boron atoms. It is expected that these yet almost unexplored compounds will reveal interesting and novel physicochemical properties. Second, adducts of imino and methano derivatives of fullerenes have the addends attached to the junctions between two six-membered rings as well as to the junctions between five- and six-membered rings ([6,6]- and [5,6]-ring junctions, respectively). Imino- and methanofullerenes are obtained by direct addition of nitrenes[1] and carbenes[5,6] to the fullerene core or through the addition of organic azides[2] and diazo compounds[5,6b,7] followed by thermal or photochemical N_2 elimination. These reactions are the only general routes that currently provide access to [5,6] adducts.[8] The synthesis of [5,6] regioisomers has proven

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* Corresponding author.

[†] Universitat de Girona.

[‡] Organon Laboratories Ltd.

[§] Universidad Complutense.

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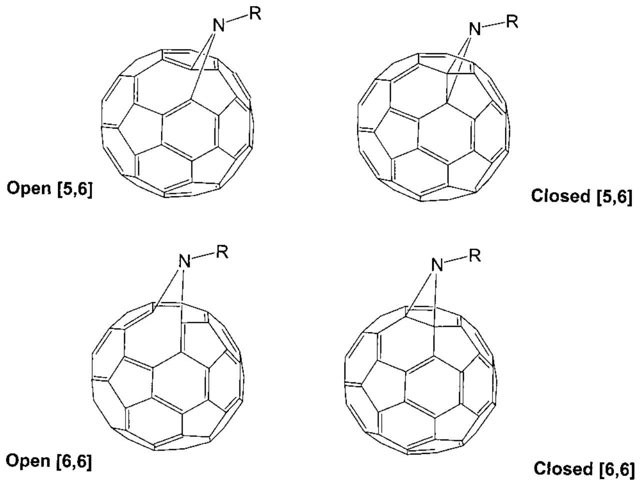
Chart 1



to be difficult given that direct additions to the [5,6]-ring junctions are uncommon in the field of fullerene chemistry.[8] To our knowledge, only a direct addition reaction to a [5,6]-ring junction of C_{60} has been reported to date.[9] Also, Meier and co-workers[10] found a direct Diels−Alder cycloaddition to the most reactive [5,6]-ring junction of C_{70}.[11]

Imino-[60]fullerenes can be obtained through two different synthetic routes. First, they can be generated through direct [2 + 1] cycloaddition to C_{60} of oxycarbonylnitrenes produced in situ either by thermal elimination of N_2 from organic azides or by base-catalyzed α-elimination of *O*-4-nitrophenylsulfonylhydroxamic acid derivatives.[1] Second, they can be formed through 1,3-dipolar cycloaddition (1,3-DC) of organic azides to C_{60} followed by thermal or photochemical N_2 extrusion.[2]

The direct oxycarbonylnitrene addition to C_{60} gives predominantly the closed [6,6]-aza-bridged regioisomers as the major regioisomer with certain amounts (ca. 10%) of the open [5,6]-aza-bridged adduct (see Chart 1). The outcome of the addition of organic azides to C_{60} depends on the nature of the azide substituent,[2b] although under thermolytic conditions, the open [5,6]-aza-bridged is usually the main adduct observed. So far, only the closed [6,6]- and open [5,6]-aza-bridged adducts have been found in these kinds of reactions. The other two possible regioisomers, the so-called open [6,6] and closed [5,6] in Chart 1, have never been observed. Computational studies show that open [6,6]- and closed [5,6]-methano and iminofullerenes are less stable than closed [6,6] and open [5,6] adducts.[12−14] Their instability is attributed to the fact that hypothetical open [6,6] or closed [5,6] structures require the introduction of three and two unfavorable double bonds in five-membered rings, respectively (see Chart 1).[8,13]

With respect to the direct oxycarbonylnitrene addition, the attack of nitrene to C_{60} seems to take place primarily at the shorter and more reactive [6,6]-ring junctions. This conclusion is supported by experimental evidence showing that singlet carbenes and silylenes are added exclusively to the [6,6]-ring junctions of C_{60} in one step.[5,8a] Less clear is the mechanistic origin of the ca. 10% of [5,6] adduct obtained. At least two hypotheses have been formulated:[1b] first, the open [5,6] product may be generated through direct addition of singlet nitrenes to [5,6]-ring junctions; second, the addition of residual triplet nitrene to C_{60} may result in a mixture of [5,6] and [6,6] regioisomers after intersystem crossover. The first hypothesis is supported by recent theoretical calculations performed in our research group.[14] Calculations have shown that the reactivities of the [5,6]- and [6,6]-ring junctions are comparable for the nitrene addition to C_{60}, both from kinetic and thermodynamic points of view, and that the most likely source of the closed [5,6]-aza-bridged adduct is the direct addition of singlet nitrenes to a [5,6] bond of C_{60}.[14]

With regard to the 1,3-DC plus thermal N_2 elimination route, experimental[2,8a] results indicate that the initial attack of the organic azide to C_{60} occurs, as usual, at the [6,6]-ring junctions, yielding a [6,6]-triazoline intermediate which sometimes can be detected or even isolated.[2a,g,l,o] In a subsequent step, the triazoline intermediate loses N_2 upon heating and forms the closed [5,6]-monoimino-[60]fullerene as the major, when not the exclusive, product. The origin of this high regioselectivity is not fully understood yet.

In a previous work, we investigated the mechanism and regioselectivity of the direct addition of singlet nitrenes to C_{60} as a synthetic route leading to monoimino-[60]fullerenes.[14] The alternative route, which is the addition of organic azides to C_{60} followed by N_2 extrusion, will be studied in this work with two main goals. First, we will compare the kinetics and thermodynamics of the [6,6] and [5,6] attacks in the initial addition of methyl azide to C_{60} in order to discuss the reasons for the preference of the [6,6] attack. Second, we will study the mechanism of N_2 elimination from the triazoline intermediate in order to elucidate the origin of the regioselectivity in the addition of alkyl azides to C_{60}.

Finally, a recent theoretical work[15] has investigated the origin of the regioselectivity in a similar reaction. In particular, Diederich and co-workers[15] studied the formation of methanofullerenes via thermal extrusion of N_2 from the pyrazoline intermediate, obtained through the addition of diazo compounds to fullerenes. The authors carried out calculations at the B3LYP/6-31G* level using benzene and pyracene as models of the fullerene core. They found that N_2 extrusion is a concerted process that takes place with an energy barrier of 15−20 kcal mol^{-1}. Diradical transition states (TS) corresponding to a possible stepwise mechanism were found to be significantly higher in energy. This study clearly brought significant findings that can be applied to the thermal extrusion of N_2 from triazolines. Some aspects of this study, however, such as the small size and the lack of carbon pyramidalization in the models used, can be criticized and may have some influence on the results.[16] For this reason, in the

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present work we preferred to study the full system, although given the size of the systems studied, a semiempirical method was used to perform geometry optimizations.

Method of Calculation

Full geometry optimizations without symmetry constraints have been carried out with the AM1 semiempirical method[17] as implemented in AMPAC 6.55,[18] a quantum chemistry program from Semichem, Inc. All zero-gradient structures have been characterized by a vibrational analysis. For some selected TSs, the AM1 intrinsic reaction path (IRP)[19] in mass-weighted Cartesian coordinates has been calculated. For all stationary points, single-point B3LYP[20] energy calculations have been performed at the AM1-optimized geometries employing the 6-31G** basis set[21] (B3LYP/6-31G**//AM1) and with the help of the Gaussian 98 program.[22] A number of theoretical studies have proven the validity of the B3LYP method combined with the 6-31G** basis set (or a similar one) to treat 1,3-DC.[23] Moreover, it has been found that AM1 provides satisfactory results for studying the 1,3-DC[24,25] and related Diels−Alder cycloadditions.[28]

Table 1. The Reaction Energies and Energy Barriers (kcal mol^{-1}) of the 1,3-DC of Methyl Azide to Ethylene at Several Levels of Theory

method	$\Delta E^{\ddagger}$ ^{a}	ΔE_r ^{a}	method	$\Delta E^{\ddagger}$ ^{a}	ΔE_r ^{a}
AM1	36.4	−25.2	B3LYP/6-311++G**	19.7	−21.7
HF/6-31G*	22.5	−32.7	MP2/6-31G*	17.8	−26.1
B3LYP/6-31G*	15.9	−27.9	MP2/6-311++G**	11.2	−25.4
B3LYP/6-31G** //AM1	27.8	−25.8	QCISD/6-31G*	24.7	−31.8

^{a} AM1 results are enthalpies.

To analyze the factors that contribute to the energy barrier in the addition of methyl azide to C_{60}, we have decomposed the AM1 and B3LYP/6-31G**//AM1 energy barriers into deformation energy (ΔE_{def}), which is needed to bring the fragments to the geometry that they adopt in the TS, and interaction energy (ΔE_{int}). This interaction energy has been, in turn, split into steric repulsion ($\Delta E°$) and orbital interaction (ΔE_{oi}) parts.[29] This latter step has been carried out using the Amsterdam Density Functional[30] (ADF) program through density functional calculations. The density functional included Becke's gradient correction[31] to the local exchange expression and Perdew's gradient correction[32] to the LDA expression (VWN[33] parametrization) for the correlation energy. A double-ς Slater-type orbital (STO) basis set extended with one polarization function was used.[34] The 1s electrons on C and N were considered as core electrons and were treated within the frozen-core approximation.[30a]

Results and Discussion

In this section, we analyze first the 1,3-DC of methyl azide to C_{60} at the [6,6]- and [5,6]-ring junctions. Then, a discussion on the N_2 elimination from the triazoline intermediate is carried out. Before starting our study in the full system, we tested the validity of the B3LYP/6-31G**//AM1 approach employed in this work by calculating the 1,3-DC of methyl azide to ethylene using different methodologies. The reaction energies and energy barriers obtained with the different methods are shown in Table 1. Taking the QCISD/6-31G* values as the reference values, one can see that reaction energies are slightly underestimated at all levels of theory except for the Hartree−Fock (HF) method. Compared to the reaction energies, larger errors are found for the energy barriers. In particular, the AM1 barrier is clearly overestimated, but the B3LYP/6-31G** single-point energy calculation at the AM1 geometry yields a reasonable result. The conclusion is that the B3LYP/6-31G**//AM1 methodology appears to be an acceptable level of calculation for obtaining reasonable estimates of reaction energies and energy barriers for 1,3-DC at low computational cost.

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(25) Compare also the AM1 results from ref 26 with the ab initio calculations of ref 27.

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Table 2. AM1 C−C Bond Distance (Å) between the Two Attacked Atoms of C_{60} Together with AM1 Standard Enthalpies of Formation (ΔH_f^0), Reaction Energies (ΔE_r), Energy Barriers ($\Delta E^‡$), and Deformation ($\Delta E_{def,C_{60}}$, $\Delta E_{def,N_3CH_3}$, and ΔE_{def}) and Interaction Energies between Deformed N_3CH_3 and C_{60} (ΔE_{int}) for the 1,3-Dipolar Cycloaddition of N_3CH_3 to C_{60}[a]

species	label	d(C−C)[b]	ΔH_f^0	ΔE_r	$\Delta E^‡$	$\Delta E_{def,C_{60}}$	$\Delta E_{def,N_3CH_3}$	ΔE_{def}	ΔE_{int}
reactant	C_{60}		973.3						
	N_3CH_3		76.7						
TS	[5,6]/6 attack I	1.537	1089.3		38.9 (46.6)	19.0 (16.8)	23.5 (30.4)	42.5 (47.2)	−3.6 (−0.6)
	[6,6] attack I	1.456	1080.2		29.8 (35.3)	12.8 (10.8)	10.6 (13.7)	23.4 (24.5)	6.4 (−10.8)
	[5,6]/6 attack II	1.548	1082.7		32.6 (34.0)	22.6 (19.7)	16.7 (25.2)	39.3 (44.9)	−6.7 (−10.9)
	[6,6] attack II	1.506	1069.3		19.1 (22.8)	25.2 (20.6)	29.9 (32.2)	55.1 (52.8)	−36.0 (−30.0)
adduct	open [5,6]/5	2.200	1054.8	4.8 (41.8)		109.9 (99.9)	44.4 (47.6)	154.3 (147.5)	−149.5 (−105.7)
	open [5,6]/6	2.208	1053.7	3.7 (41.8)		111.5 (101.3)	45.5 (48.6)	157.0 (149.9)	−153.3 (−109.1)
	open [6,6]	2.231	1047.6	−2.4 (31.1)		148.0 (124.4)	44.9 (47.0)	192.9 (171.4)	−195.3 (−140.3)
	closed [5,6]/5	1.692	1045.2	−4.8 (17.0)		60.6 (52.8)	51.3 (56.6)	111.9 (109.4)	−116.7 (−92.4)
	closed [5,6]/6	1.698	1044.9	−5.2 (12.6)		61.6 (47.3)	51.4 (56.7)	113.0 (104.0)	−118.1 (−105.5)
	closed [6,6]	1.631	1027.1	−23.0 (−2.1)		56.3 (48.2)	52.5 (58.6)	108.8 (106.8)	−131.7 (−108.9)

[a] AM1 energy values are enthalpies. All energy values are given in kcal mol^{-1}. Values in parentheses have been recalculated at the B3LYP/6-31G**//AM1 level. [b] The experimental [6,6] and [5,6] bond lengths in C_{60} are 1.401 and 1.458 Å, whereas the AM1-optimized bond lengths are 1.385 and 1.464 Å, respectively.

Increasing the size of the basis set has an unclear effect on the energy barriers, differing for the MP2 and B3LYP methodologies. When a move from the 6-31G* basis set up to 6-311++G** is made, the energy barrier decreases at the MP2 level and increases at the B3LYP level.

1,3-Dipolar Cycloaddition of Methyl Azide to C_{60}. The pioneering work of Huisgen[35] provided a general definition of 1,3-DC in which the 1,3-dipole, represented by a zwitterionic species, reacts with a dipolarophile molecule containing a multiple bond to form five-membered heterocyclic systems. The minor effect of solvent polarity on the reaction rate, together with the high regioselectivity observed, has provided support for a concerted reaction pathway.[36] This result was reinforced by the landmark study at the MCSCF level of Schlegel and co-workers[37] and by a number of calculations on 1,3-DC reactions performed with semiempirical and ab initio methods.[24,27,38] For this reason, in the present work only the concerted mechanism has been analyzed.

The AM1 standard enthalpies of formation of reactants, TSs, and adducts, together with reaction energies, energy barriers, and deformation and interaction energies for the different 1,3-DC attacks of methyl azide to C_{60} are collected in Table 2. The geometries of the different adducts and TSs identified are depicted in Figures 1 and 2, respectively. The attack of methyl azide to C_{60} may produce the six regioisomers depicted in Figure 1, corresponding to the [6,6] and [5,6] isomers that can be considered either open or closed depending on the final C−C bond distance of the attacked bond. The bond lengths between the two attacked carbon atoms in the open structures are about 2.2 Å at the AM1 level. In contrast, this C−C bond distance in closed structures ranges from 1.6 to 1.7 Å (see Figure 1) at the AM1 level, corresponding to a slightly elongated C−C single bond. The AM1 structure of the closed [6,6]-$C_{60}N_3CH_3$ is similar to the previously reported X-ray structure of 1′-(2-methoxyethoxymethyl)triazolinyl[4′,5′:1,2]-1,2-dihydro-[60]fullerene. The C−C bond length of the two fullerene carbon atoms attacked is 1.574 Å in the X-ray structure and 1.631 Å in the AM1-optimized $C_{60}N_3CH_3$ species. The distortion of the fullerene cage is reflected by the bond length deviations of the C═C double bonds from the mean average value (X-ray, 1.385 Å; AM1, 1.383 Å) and correlates very well with the experimental data. The average bond lengths of the AM1 structure for the cis-1 (1.369 Å) and e (1.384 Å) bonds match perfectly those of the X-ray structure for the same cis-1 (1.362 Å) and e (1.383 Å) bonds.

In the case of the [5,6] regioisomer, two possible structures exist, the so-called [5,6]/5 and the [5,6]/6. In the [5,6]/5 structure, the methyl group faces the pentagonal ring, whereas in the [5,6]/6 structure the methyl group faces the hexagonal ring (see Figure 1). Among the possible adducts, the closed [6,6] is the most stable by about 20 kcal mol^{-1}, followed by the open [5,6]/6. In fact, the reaction leading to the closed [6,6] regioisomer is the only one that is exothermic at the B3LYP/6-31G**//AM1 level. This is not surprising, considering that the regiochemistry of the addition reactions to fullerenes is governed by the trend to minimize the energetically unfavorable double bonds in pentagonal rings.[8] As can be observed in Chart 1, open [6,6] and closed [5,6] isomers require the introduction of three and two double bonds, respectively, in five-membered rings.[13] The open [5,6] regioisomer can avoid locating double bonds in pentagonal rings but only at the expense of placing double bonds at the bridgehead atom, violating Bredt's rule. Therefore, it is not unexpected that at both the AM1 and B3LYP/6-31G**//AM1 levels the most stable $C_{60}(N_3CH_3)$ regioisomer is the closed [6,6] adduct.

With respect to the TSs, we have analyzed two differ-

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(35) (a) Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 565. (b) Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 633.

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(38) Sustmann, R.; Sicking, W.; Huisgen, R. *J. Org. Chem.* **1993**, *58*, 82.

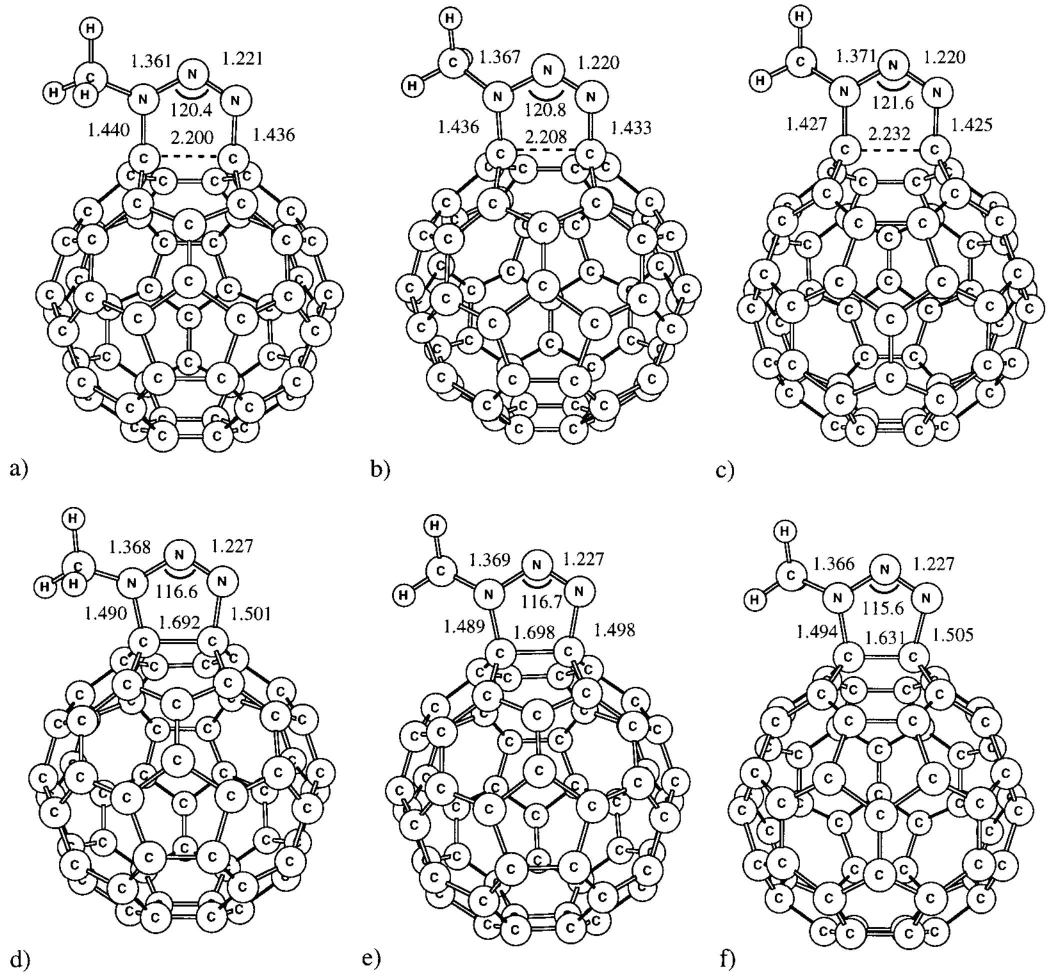

Figure 1. The six possible AM1 regioisomers that can be obtained in the 1,3-DC of methyl azide to C_{60}: (a) the open [5,6]/5, (b) the open [5,6]/6, (c) the open [6,6], (d) the closed [5,6]/5, (e) the closed [5,6]/6, and (f) the closed [6,6].

ent attacks. The attack labeled I has a TS in which the length of the C−N bond being formed (corresponding to the unsubstituted N atom) is shorter than the C−N bond distance of the N atom bearing the methyl substituent. The reverse is true for the attack labeled II (see Figure 2). Attack II is favored by about 10 kcal mol^{-1}, in agreement with the fact that the calculated Fukui function[39] measuring the reactivity of methyl azide toward an electrophilic reagent (C_{60}) shows a larger contribution of the substituted N atom (figure not shown). An opposite situation is encountered for the TSs of asymmetric Diels−Alder cycloadditions, in which the bond with the carbon atom bearing the substituent stretches whereas the forming bond with the unsubstituted atom contracts.[40] Remarkably, previous PM3 calculations on the 1,3-DC of *N*-methylazomethine ylide to the [6,6] bonds of C_{70} also yielded high asynchronous TSs.[41] Finally, the IRP from the TS in attack II to the [6,6]-ring junction (Figure 2d) was constructed to confirm that the TS indeed connects the reactants with the triazoline intermediate (Figure 1f).

For the [5,6]-addition, we have located only the TS corresponding to the [5,6]/6 adduct. The [6,6] addition is preferred over the [5,6] attack by ca. 10 kcal mol^{-1}, indicating that the addition of methyl azide to C_{60} yields only the closed [6,6]-triazoline intermediate through a [6,6] attack of type II. Experimentally, this [6,6]-triazoline intermediate has been detected and even isolated in some 1,3-DCs of organic azides to fullerenes.[2a,g,l,o] The results obtained are not surprising, taking into account that most reactants add to the junction between two six-membered rings of C_{60}, where the electron density is higher.[8,42]

It is of interest to analyze the origin of the difference between the barriers associated with attacks of type II at the [6,6]- and [5,6]-ring junctions. For this purpose, we have divided the energy barrier of each 1,3-DC into deformation energy and interaction energy ($\Delta E^{\ddagger}_{1,3-\mathrm{DC}} = \Delta E^{\ddagger}_{\mathrm{def}} + \Delta E^{\ddagger}_{\mathrm{int}}$). The deformation energy has been split, in turn, into the deformation energies of methyl azide and C_{60} ($\Delta E^{\ddagger}_{\mathrm{def}} = \Delta E^{\ddagger}_{\mathrm{def,CH_3N_3}} + \Delta E^{\ddagger}_{\mathrm{def,C_{60}}}$). Table 2 shows that the total deformation energy is larger for the attack at the [6,6]-ring junction, especially because of the higher energy needed to close the ∠NNN angle of methyl azide

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(39) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.

(40) (a) Houk, K. N. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 682. (b) Solà, M.; Ventura, M.; Segura, C.; Duran, M. *J. Chem. Soc., Perkin Trans. 2* **1995**, 605.

(41) Langa, F.; de la Cruz, P.; de la Hoz, A.; Espíldora, E.; Cossío, F. P.; Lecea, B. *J. Org. Chem.* **2000**, *65*, 2499.

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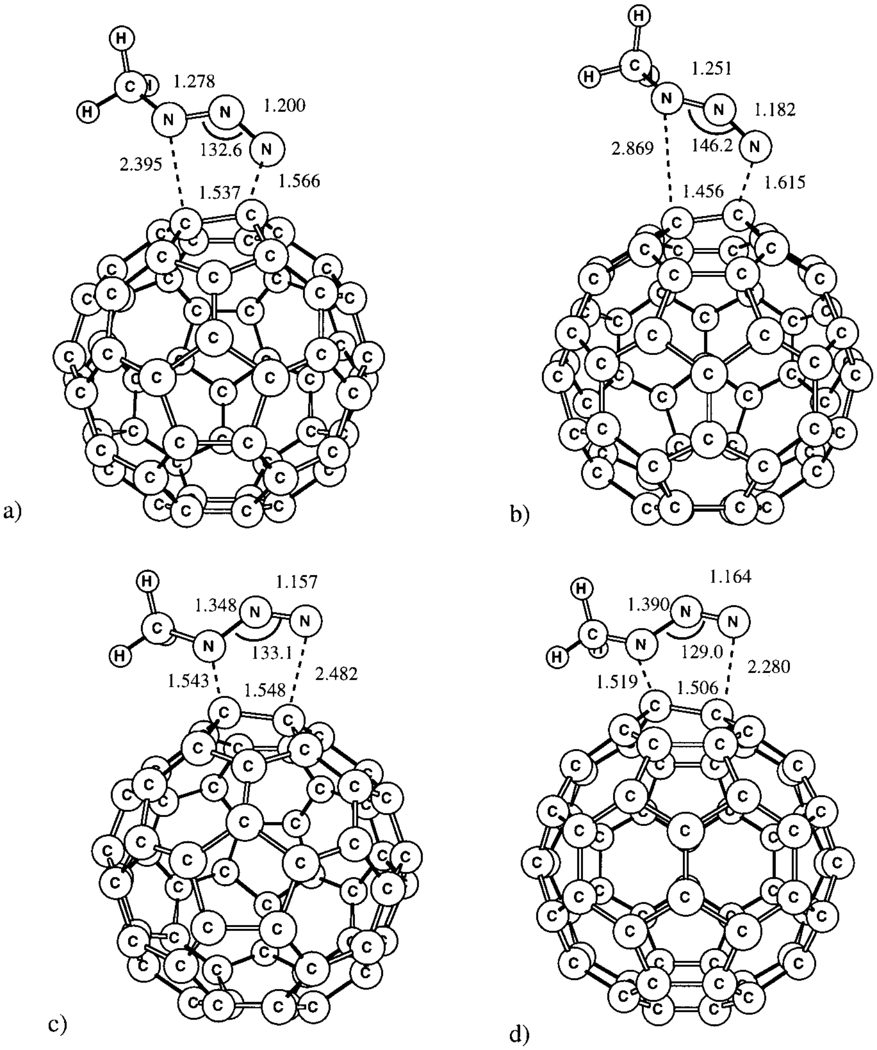

Figure 2. AM1 transition states corresponding to the four studied attacks in the 1,3-DC of methyl azide to C_{60}: (a) the TS of the [5,6]/6 attack I, (b) the TS of the [6,6] attack I, (c) the TS of the [5,6]/6 attack II, and (d) the TS of the [6,6] attack II.

in this attack (see Figure 2).[43] However, the main difference comes from the interaction energy that favors the [6,6] attack by more than 20 kcal mol^{-1}. This interaction energy has two main components, namely, the steric repulsion (Pauli repulsion + electrostatic interactions) and the orbital relaxation (polarization + charge-transfer effects).[29] The decomposition of the interaction energy into the steric repulsion and the orbital relaxation terms has been carried out at the BP86/DZP//AM1 level using the ADF program. The results show that the steric repulsion is smaller for the [5,6] attack by only 3.5 kcal mol^{-1}, whereas the orbital relaxation term favors the [6,6] addition by 21.1 kcal mol^{-1} because of better overlaps between the frontier orbitals in the [6,6] attack, especially between those involved in the charge transfer from C_{60} to methyl azide. In fact, the flows of electronic charge from C_{60} to methyl azide and from methyl azide to C_{60} increase in the [6,6] addition when compared to the [5,6] attack, but the enhancement is more remarkable for the transfer from C_{60} to methyl azide. As a result, the whole charge transfer from methyl azide to C_{60} is slightly smaller in the [6,6] attack than in the [5,6] addition (0.17 vs 0.21 e, respectively, at the BP86/DZP//AM1 level).

In summary, it can be concluded that the 1,3-DC of methyl azide to C_{60} takes place at the [6,6]-ring junctions, giving rise to a closed [6,6]-triazoline intermediate. The main reason for the preference of the [6,6] over the [5,6] attack is the more favorable orbital interactions through better overlaps between frontier orbitals in the [6,6] addition. Therefore, for the study of the next reaction step (the N_2 extrusion from the triazoline intermediate), only the closed [6,6]-triazoline intermediate has been considered.

Thermal N_2 Extrusion from the Triazoline Intermediate. From an experimental point of view, the isolation of the triazoline intermediate is possible when the reaction is performed at highly concentrated solutions of the reactants and moderate reaction temperatures (ca. 60 °C).[2,3] At slightly higher temperatures (100 °C), thermal elimination of N_2 takes place, leading almost exclusively to the open [5,6] product.[1c,d,2] In contrast, photolysis of the triazoline intermediate produces an isomeric mixture of open [5,6]- and closed [6,6]-monoimino-[60]fullerene.

Recent theoretical studies by Wallenborn et al.[15] have shown that in the dinitrogen extrusion from 7,8-diazabicyclo[5.3.0]nona-2,4,7-triene, diradical TSs and intermediates are higher in energy than concerted TSs.

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[43] The AM1-optimized $\angle$NNN angle of free methyl azide is 168.7°.

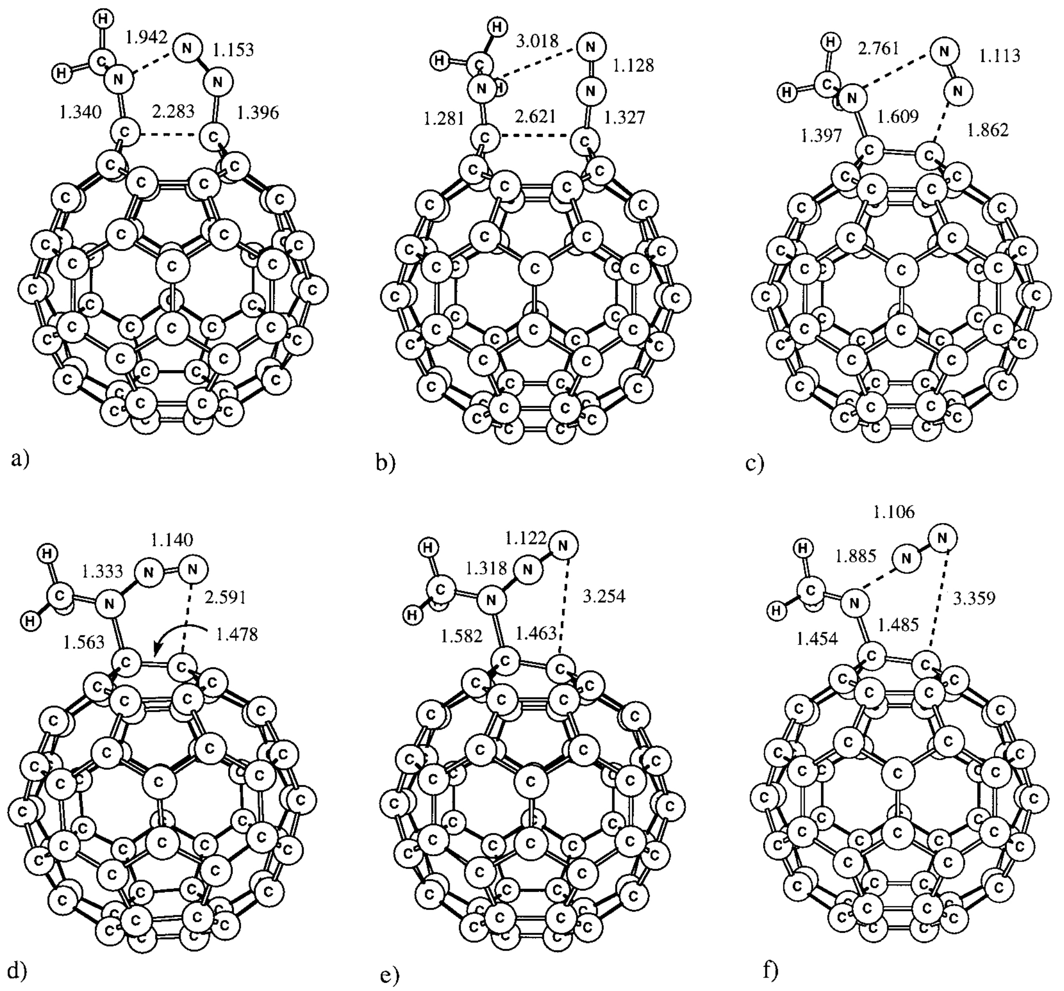

Figure 3. AM1 intermediates and transition states related to the N2 extrusion from the closed [6,6]-triazoline intermediate: (a) TS1, (b) INT1, (c) TS12, (d) TS2, (e) INT2, and (f) TS21.

According to these results, our initial searches for TSs were limited to concerted TSs. At the AM1 level, two TSs corresponding to the thermal extrusion of dinitrogen from the triazoline intermediate were located. In the TS denoted TS12, the cleavage of the N−N single bond precedes the breaking of the C−N bond. The order of the two cleavages is the opposite for the TS named TS21 (see Figure 3). Vibrational analyses verified that both are first-order saddle points corresponding to the extrusion of dinitrogen. At the AM1 level, both TSs have similar energy barriers (see Table 3). However, B3LYP/6-31G*//AM1 calculations favor TS12 by more than 10 kcal mol^{-1}, in agreement with experimental results suggesting that cleavage of the N−N single bond precedes cleavage of the C−N bond in the thermolysis of triazolines.[2b,44] Theoretical results on the ozonolysis reaction also indicate that in the primary ozonide intermediate, the O−O single-bond breaking precedes the C−O cleavage.[23h,26,27] In the two TSs, the extrusion of dinitrogen proceeds in a highly asynchronous fashion. The geometry of TS12 is similar to that reported by Wallenborn et al.[15] in a pyracene intermediate, taken as a model system of the pyrazoline formed when diazomethane adds to C_{60}. Moreover, the energy barrier for TS12 is almost identical to the energy barriers found at the B3LYP and CCSD(T) levels for the elimination of nitrogen in the pyrazoline intermediate formed in the addition of diazomethane to ethylene.[23d]

To confirm that TS12 and TS21 are connected to the closed [6,6]-triazoline intermediate and to the aziridine product, the IRPs starting from these TSs were constructed. Interestingly, it was found that the two TSs are connected to the open [5,6]-aziridine adduct. The geometry of these TSs already suggests that the thermal N_2 loss occurs simultaneously with the formation of the new C−N bond. One should expect that the delocalization of spin density within the six-membered ring as the loss of N_2 proceeds may result in the synthesis of both [6,6] and [5,6] adducts. However, the evolution of TS12 or TS21 along the IRP shows that the N_2 molecule sterically prevents the nitrene substituent from adding to the originally attacked [6,6] bond and forces the nitrene substituent to attack either of the two adjacent [5,6]-ring junctions. Therefore, it seems plausible that the possible formation of [6,6] adducts depends on the timing of the dinitrogen molecule's liberation. The IRPs show that the thermal loss of N_2 occurs at the same time as C−N bond formation, and thus only the [5,6] isomer can be formed. This is in agreement with experimental findings and in line with previous mechanistic suggestions by Diederich and co-workers,[7i] Shen et al.,[2b] and Schick and Hirsch.[7k] In contrast, for the photochemical process the N_2 loss is presumed to yield a relatively stable diradical intermedi-

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(44) Scheiner, P. *Selective Organic Transformations*; Thyagarajan, B. S., Ed.; Wiley: New York, 1970; Vol. 2, p 327.

Table 3. AM1 C−C Bond Distance (Å) between the Two Attacked Atoms of C_{60} Together with AM1 Standard Enthalpy of Formation (ΔH_f^0), Reaction Energies (ΔE_r), Energy Barriers ($\Delta E^{\ddagger}$), and Deformation ($\Delta E_{def,C_{60}}$, $\Delta E_{def,NCH_3}$, and ΔE_{def}) and Interaction Energies between Deformed NCH_3 and C_{60} (ΔE_{int}) of the Species Involved in N_2 Elimination from the Triazoline Intermediate[a]

species	label	d(C−C)[b]	ΔH_f^0	ΔE_r [c]	$\Delta E^{\ddagger}$ [d]	$\Delta E_{def,C_{60}}$	$\Delta E_{def,NCH_3}$	ΔE_{def}	ΔE_{int}
triazoline	closed [6,6]	1.631	1027.1						
TS′	TS1	2.283	1073.8		46.8 (45.0)				
	TS2	1.478	1072.2		45.2 (34.4)				
intermediate	INTl	2.621	1038.3		11.3 (39.4)				
	INT2	1.463	1069.3		42.3 (49.3)				
TS″	TS12	1.485	1091.0		64.0 (47.1)				
	TS21	1.609	1088.9		61.9 (57.2)				
adduct + N_2[e]	open [5,6]/5	2.175	998.2	−28.8 (−29.8)		87.7 (80.0)	5.8 (4.9)	93.5 (84.9)	−122.3 (−114.7)
	open [5,6]/6	2.174	996.8	−30.2 (−27.6)		87.5 (79.6)	5.4 (4.2)	92.9 (83.8)	−123.1 (−111.4)
	open [6,6]	2.160	1011.1	−15.9 (−20.8)		123.1 (118.7)	5.5 (3.5)	128.6 (122.2)	−144.5 (−143.0)
	closed [5,6]/5	1.620	1019.9	−18.3 (−24.2)		28.9 (24.7)	4.9 (4.3)	33.8 (29.0)	−52.1 (−53.2)
	closed [5,6]/6	1.620	1020.4	−6.6 (−13.5)		28.1 (18.7)	4.9 (4.3)	33.0 (23.0)	−39.6 (−36.5)
	closed [6,6]	1.559	999.3	−27.7 (−33.6)		26.0 (25.8)	4.8 (4.3)	30.8 (30.1)	−58.5 (−63.7)

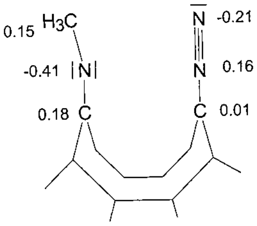
[a] AM1 energy values are enthalpies. All energy values are given in kcal mol^{-1}. Values in parentheses have been recalculated at the ab initio B3LYP/6-31G**//AM1 level. Relative values refer to the closed [6,6]-triazoline intermediate. [b] The experimental [6,6] and [5,6] bond lengths in C_{60} are 1.401 and 1.458 Å, whereas the AM1-optimized bond lengths are 1.385 and 1.464 Å, respectively. [c] Reaction energies refer to the triazoline intermediate. [d] The energy barriers for TS1 and TS2 refer to the triazoline intermediate, whereas the energy barriers of TS12 and TS21 refer to INT1 and INT2, respectively. [e] $\Delta H_f^0(N_2)$ = 11.2 kcal mol^{-1}.

ate that ultimately produces a mixture of [5,6] and [6,6] regioisomers.

To our surprise, the IRPs from TS12 and TS21 do not connect these TSs directly with the closed [6,6]-triazoline intermediate but with the intermediates named INT1 and INT2, respectively (see Figure 3). The transition states that link INT1 and INT2 with the closed [6,6]-triazoline intermediate are TS1 and TS2, respectively. The existence of INT2 is not supported by the B3LYP/6-31G**//AM1 results. This is not unexpected because it is known that semiempirical calculations tend to favor stepwise over concerted mechanisms.[24,38] However, INT1 is stable according to the B3LYP/6-31G**//AM1 calculations. To analyze the possible diradical nature of INT1, unrestricted calculations at the same level of theory (UB3LYP/6-31G**//AM1) were performed. The approximate wave function constructed from the Kohn−Sham orbitals was an almost pure singlet with an S^2 value of 3 × 10^{-4} au. The distribution of spin density shows that INT1 is not a diradical, the atomic spin density on each atom being always <10^{-2} au. Instead, the electronic distribution in INT1 is more consistent with a zwitterionic structure (see Chart 2). Because of that, one can predict that INT1 will be stabilized by polar solvents. Remarkably, the N−N bond length of this intermediate at the AM1 level is 1.128 Å, not far from the 1.106 Å found in free N_2.

It is interesting to discuss the relative stability of the six possible monoimino-[60]fullerene regioisomers drawn in Figure 4. As said before, the final product is the open [5,6] adduct and, in particular, the open [5,6]/6 adduct. The open [5,6]/6 and open [5,6]/5 regioisomers have similar energies. The open [5,6]/6 is about 1.5 kcal mol^{-1} more stable than the open [5,6]/5 at the AM1 level, whereas the B3LYP/6-31G**//AM1 results give the open [5,6]/5 as the most stable. The higher stability of the [5,6]/5-iminofullerene agrees with the fact that in the parent [5,6]-bridged methanofullerenes the diastereomer with the bulkier substituent located above the five-membered ring seems to be the most abundant in the reaction mixture.[7a,j,k] We have not located the TS for the pyramidal inversion that connects the open [5,6]/6 and open [5,6]/5 systems, although experimental NMR studies suggest that this process is almost barrierless.[2a]

Chart 2. B3LYP/6-31G//AM1 Mulliken Charges on the Most Relevant Atoms of INT1[a]**



[a] 0.15 is the charge on the methyl group.

The other four possible adducts (the open [6,6], the closed [5,6]/5, the closed [5,6]/6, and the closed [6,6]) are also minima in the AM1 potential energy surface of $C_{60}(NCH_3)$. As found for the triazoline intermediates (Table 2), the closed [5,6] and open [6,6] adducts are the less stable regioisomers. Open [6,6] and closed [5,6] isomers require the introduction of three and two unfavorable double bonds, respectively, in five-membered rings.[13] The open [5,6] regioisomer can avoid locating double bonds in pentagonal rings but only at the expense of placing double bonds at the bridgehead atom, violating Bredt's rule (see Chart 1). Therefore, it is not unexpected that at the B3LYP/6-31G**//AM1 level the most stable $C_{60}(NCH_3)$ regioisomer is the closed [6,6] adduct, in agreement with the experimental results showing that the

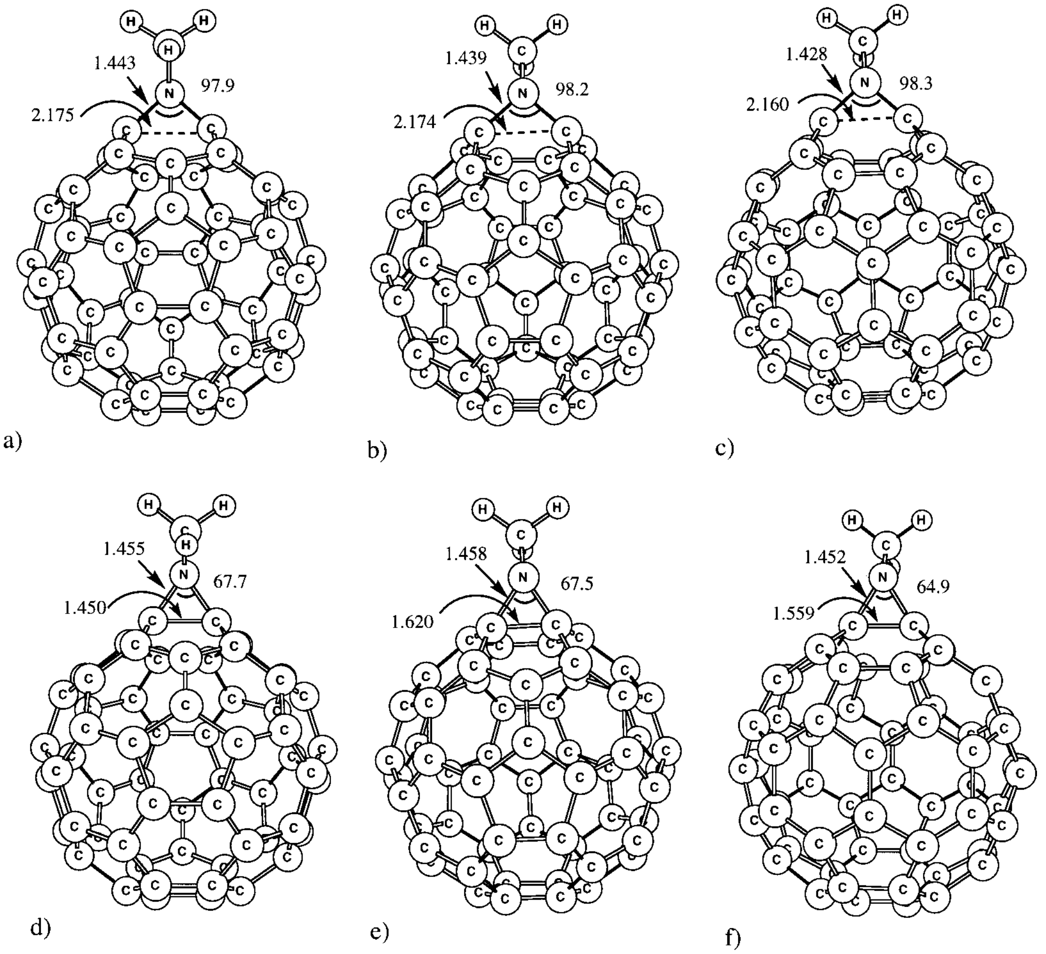
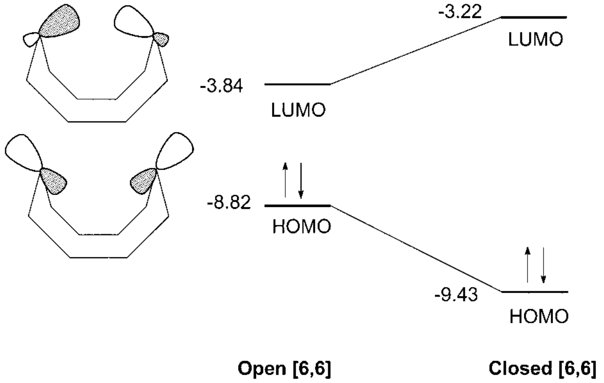


Figure 4. The six possible AM1 regioisomers of methylimino-[60]fullerene: (a) the open [5,6]/5, (b) the open [5,6]/6, (c) the open [6,6], (d) the closed [5,6]/5, (e) the closed [5,6]/6, and (f) the closed [6,6].

closed [6,6]-methanofullerenes are more stable than the open [5,6] isomers.[5,7g,i,j] The preferred formation of the thermodynamically less stable open [5,6] product suggests that loss of N_2 proceeds under kinetic control, as suggested previously[2b,7i,k] for the N_2 loss in pyrazolines. In contrast to the B3LYP/6-31G**//AM1 result, the AM1 method gives the open [5,6]/6 adduct as the most stable. This is an indication that the AM1 method overestimates the stability of fullerene structures with open bonds, as noted previously by Clark et al.[2d] and by Diederich and co-workers.[13]

The closed [6,6] regioisomer is usually the most stable adduct in cycloaddition reactions to C_{60}. The only exception is the open [5,6] adducts in $C_{60}(NCH_3)$, which have a similar stability to that of the closed [6,6] adduct. Further insight into the origin of the different relative stabilization of the open [5,6] adducts in $C_{60}(NCH_3)$ and $C_{60}(N_3CH_3)$ can be gained by decomposing the reaction energy into deformation and interaction energies (see Tables 2 and 3). From the analysis of these values, it is possible to draw the following five general conclusions: (a) As expected, the deformation energy of the fullerene core is larger for C_{60} with open bonds than for closed fullerene fragments. (b) The smaller ∠NNN angle explains the larger deformation energy needed to distort N_3CH_3 in closed C_{60} fragments as compared to open C_{60} structures, whereas the deformation of NCH_3 is similar for open and closed fullerene fragments. (c) Remarkably, to open a [6,6] bond is energetically more demanding than to open a [5,6] bond by about 30 kcal mol^{-1}, and this can be attributed to the fact that open [6,6] structures require the introduction of three double bonds in five-membered rings as opposed to two double bonds for an open [5,6] structure. (d) The interaction energies are higher for open than for closed C_{60} systems because the HOMO and LUMO orbitals of the C_{60} fragment are destabilized and stabilized, respectively, when going from closed to open

Chart 3. AM1 Frontier Orbitals for the Open and Closed [6,6]-C_{60} Fragments of the Corresponding Aziridine Regioisomers (Figure 1c,f)[a]



[a] These orbitals are almost completely localized in the two carbon atoms being attacked. Energies are given in eV. For comparison purposes, the AM1 energies of the HOMO and LUMO of free C_{60} are −9.64 and −2.65 eV, respectively.

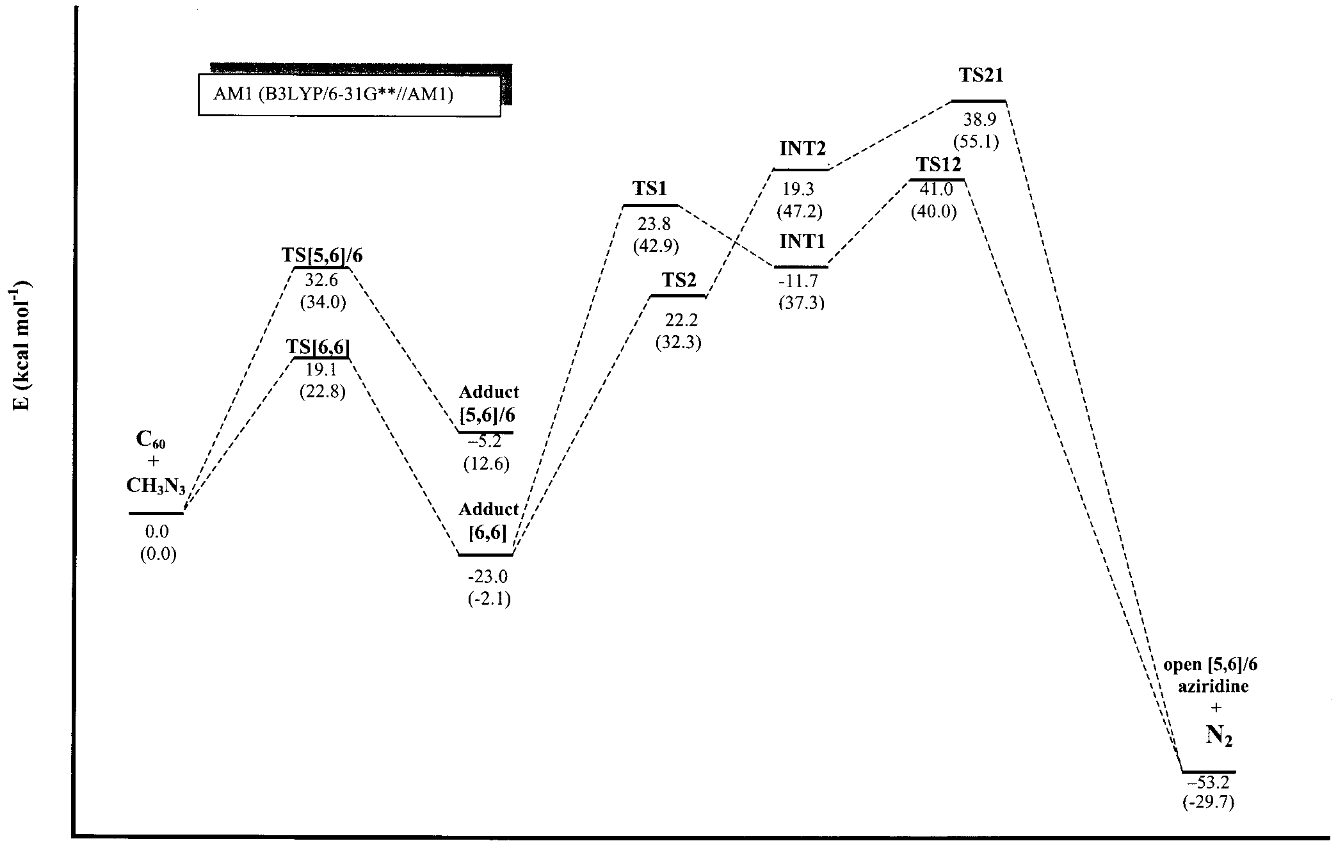


Figure 5. Energy profile (in kcal mol^{-1}) for the whole reaction (1,3-DC plus N_2 extrusion).

structures (see Chart 3). (e) The interaction energies are also higher for the addition of N_3CH_3 to open or closed C_{60} fragments as compared to those of NCH_3. This can be understood by taking into account the shape of the frontier orbitals of N_3CH_3 and NCH_3 (depicted for instance in ref 45). In particular, the HOMO(C_{60})−LUMO(N_3CH_3) interaction is much more efficient than the corresponding HOMO(C_{60})−LUMO(NCH_3) interaction. The key factor that contributes to the important stabilization of the open [5,6] adducts in $C_{60}(NCH_3)$ is, however, the interaction energy, which in comparison to that of the closed [6,6] adduct is 64.6 kcal mol^{-1} (47.7 at the B3LYP/6-31G**//AM1 level) larger for the open [5,6]/6-$C_{60}(NCH_3)$ regioisomer, whereas for the $C_{60}(N_3CH_3)$ species this difference is only 21.6 kcal mol^{-1} (0.2 at the B3LYP/6-31G**//AM1 level). The reason for the more favorable interaction energy in the open [5,6]/6-$C_{60}(NCH_3)$ regioisomer can be found in the short distance between the N atom and the center of the C−C bond being attacked in the open structures, which favors better overlap among frontier orbitals and stabilizes the open structures as compared to the closed ones in $C_{60}(NCH_3)$. It is also possible to predict that nitrenes with bulky substituents may thermodynamically destabilize the open [5,6] regioisomers and favor the closed [6,6] species.

Conclusions

Figure 5 depicts the complete B3LYP/6-31G**//AM1 energy profile for the 1,3-DC reaction of methyl azide to C_{60} followed by N_2 elimination to form methylimino-[60]-fullerenes. The lowest energy path involves addition of methyl azide to the [6,6]-ring junctions to yield a stable closed [6,6]-triazoline intermediate. Our calculations confirm that this intermediate is stable enough to be isolated when working at mild conditions.[3] Loss of N_2 requires higher temperatures because the energy needed to reach TS1 from the triazoline intermediate is about 45 kcal mol^{-1}. Our results suggest a stepwise mechanism in which, the N−N single bond is first broken to give INT1 and the cleavage of the C−N bond then occurs to yield the open [5,6]-methylimino-[60]fullerene. At the B3LYP/6-31G**//AM1 level, the INT1 is a stable compound with an activation energy barrier of only ca. 3 kcal mol^{-1} for the reaction that converts this intermediate to the aziridine product. As a consequence, our results show that INT1 should be very difficult to isolate or even detect. Moreover, it is difficult to predict whether this intermediate would be found stable or not at higher levels of theory because INT1 is located in a very shallow minimum. As a whole, although our calculations support a stepwise mechanism, it is not yet possible to draw a definite conclusion on the kind of mechanism (either stepwise or concerted) that operates in the N_2 extrusion step.

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