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Pyrimidine *ortho*-quinodimethanes. Part 2: Synthesis of new [60]fullerene adducts based on substituted pyrimidine derivatives and their ^{1}H NMR dynamic study

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ABSTRACT

The Diels–Alder reaction of various pyrimidine *ortho*-quinodimethanes generated in situ with C_{60} gives access to a variety of new fullerodihydroquinazoline derivatives. This variety is increased since substituents on the pyrimidine ring can be easily modified before or after its reaction with C_{60}. Variable temperature ^{1}H NMR spectra provided thermodynamic parameters related to the boat-to-boat interconversion of the cyclohexene ring fused to the fullerene moiety. The mass spectra of the prepared cycloadducts show that the retro-Diels–Alder process takes place easily with elimination of the corresponding diene molecule.

1. Introduction

Fullerene derivatives have been extensively studied due to the outstanding properties they exhibit.[1] Thus, for instance, pyrrolidinofullerenes[2] as well as fullerene-stoppered molecular shuttles[3] have non-linear optical properties. Since fullerenes are known to show remarkable electron accepting properties, they have been covalently and supramolecularly connected to a wide variety of electron donating species to form donor–acceptor dyads with interesting photoinduced electron transfer processes, thus mimicking the photosynthetic process.[4] Furthermore, photovoltaic devices have been prepared from semiconducting π-conjugated oligomers and some fullerene derivatives, mainly from the well-known PCBM.[5] On the other hand, ambipolar organic field effect transistor has been fabricated, for instance, from thioxanthene–fullerene dyad systems.[6] Substituted fullerene derivatives with appropriate functional groups can be also used to form supramolecular ensembles through hydrogen bonds[7] or other motifs.[8] Heterocyclic fullerene derivatives, mainly prepared by 1,3-dipolar cycloaddition reactions involving fullerenes as dienophiles, have been extensively studied as one of the most versatile procedures to prepare fullerene derivatives.[9]

An alternative synthetic approach to homo- and heterocyclic fused fullerenes has involved the use of Diels–Alder reactions of suitably functionalized *ortho*-quinodimethanes (*o*-QDMs) as dienes and C_{60} or C_{70} as dienophiles.[10] In particular, heterocyclic *ortho*-quinodimethanes, generated in situ from appropriate precursors, are highly reactive dienes used frequently in this cycloaddition process. Thus, the thermolysis of adequate bis(bromomethyl)pyrazine derivatives [11] or pyrazine-fused sultines[12] in the presence of C_{60} affords the corresponding pyrazine-fused fullerenes. In addition, pyrimidine-fused fullerenes have been prepared by Diels–Alder reaction from substituted pyrimidine *ortho*-quinodimethanes (*o*-QDMs) generated by thermal extrusion of sulfur dioxide of the corresponding pyrimidine-fused 3-sulfolenes.[13] Higher-fullerene derivatives were also prepared by DA reaction of C_{70} and C_{76} with *o*-QDMs generated in situ.[14]

We report herein a synthetic procedure for the preparation of new dihydroquinazoline-fused fullerene (Scheme 1) based on the easy generation of 2,4-functionalized pyrimidine *ortho*-quinodimethanes by heating the corresponding 2,4-disubstituted

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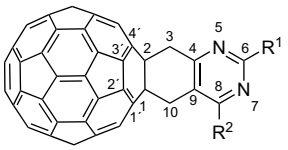
cyclobutapyrimidines, which are, in turn, prepared from cyclobutanone and different nitriles. This versatile proposed approach provides a diverse set of products and allows to prepare fullerene derivatives with functional groups, which can be easily transformed.



Scheme 1. Numbering used in the text.

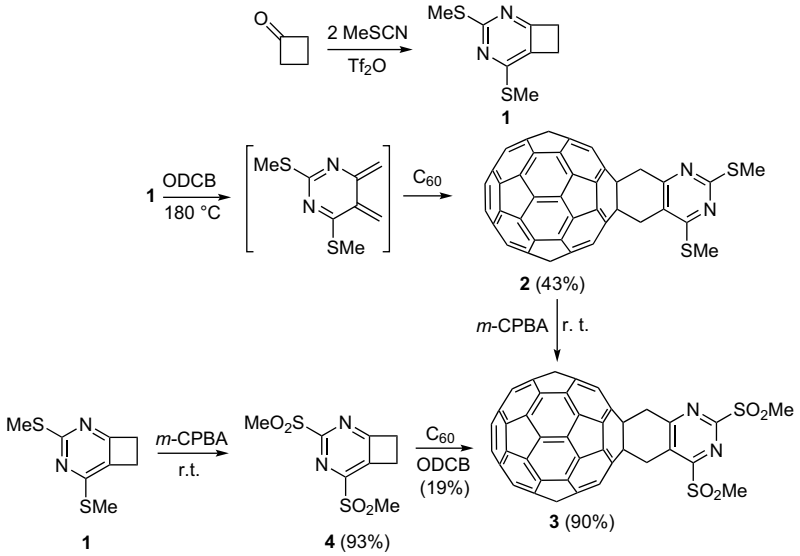
2. Results and discussion

Following our general method for the synthesis of pyrimidines,[15] the reaction of cyclobutanone with methylthiocyanate and triflic anhydride (Scheme 2) affords 2,4-bis(methylsulfanyl)-5,6-dihydrocyclobuta[*d*]pyrimidine **1**.[15,16] The thermolysis of **1** with C_{60} in *ortho*-dichlorobenzene (ODCB) at 180 °C produces cycloadduct **2** in moderate yield via the corresponding *ortho*-quinodimethane intermediate. We have previously reported the use of this procedure to obtain 2,4-dimethyl- and 2,4-diphenylsubstituted pyrimidine cycloadducts.[17] However, cycloadduct **2** bears functional groups capable of further chemical transformations to afford a new assortment of fullerene derivatives. Thus, the reaction of **2** with *m*-CPBA under mild conditions leads to the formation of cycloadduct **3** in very good yield (Scheme 2). It should be noted that the extremely low solubility of compound **3** makes it impossible to record its NMR spectra in liquid phase. An alternative synthetic approach to cycloadduct **3** consists of the modification of the pyrimidine derivative **1** before its reaction with C_{60}. Thus, 2,4-bis(methylsulfanyl)cyclobutapyrimidine **1** can undergo a mild oxidation to **4** in almost quantitative yield, which then reacts with C_{60} to form the cycloadduct **3** in a significant lower yield. The fact that the oxidation can take place before or after the Diels–Alder cyclization confers considerable versatility to this procedure. The Diels–Alder reaction is controlled by the energy differences between HOMO (diene) and LUMO (dienophile). These energies are closely related to the electronic nature of the substituents attached either to the diene or dienophile. Scheme 3 indicates that C_{60} possesses a relatively low energy LUMO, which facilitates the cycloaddition (in the scheme the LUMO energy values of other widely used dienophiles are included for comparison). In contrast, the *ortho*-quinodimethane derived from **4** bearing the electron withdrawing $-SO_2Me$ groups exhibits an unfavourable HOMO energy value for the DA cycloaddition, thus accounting for the lower yield obtained in the reaction of **4** with C_{60}.

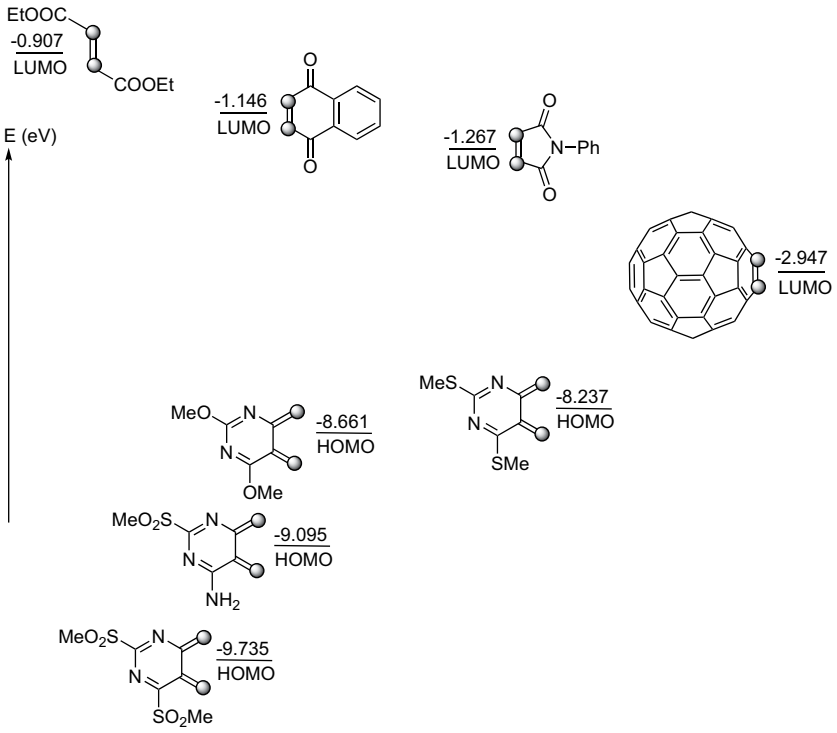
As we have previously reported,[16] the methylsulfonyl groups attached to the pyrimidine ring can be easily transformed into other functional groups whose electronic character allows an easier Diels–Alder process. Thus, using as starting material the aminomethylsulfonyl derivative **5**, the corresponding cycloadduct **6** is obtained in moderate yield (Scheme 4) as a result of a narrower HOMO–LUMO energy difference. Unfortunately, the low solubility of **6** limits its use for further synthetic applications. In order to study the cycloadducts whose solubilities permit to record their NMR spectra in liquid phase, we prepared the dimethoxycyclobutapyrimidine **7** from **4** by nucleophilic substitution of the methylsulfonyl groups with sodium methoxide.[16] Compound **7** reacts with C_{60} to form the corresponding cycloadduct **8** (Scheme 4). The acid hydrolysis of the dimethoxy cycloadduct **8** with 6 M HCl led to the formation of the uracil fullerene derivative **9** in a straightforward manner. Although the uracil derivative resulted to be poorly soluble in common organic solvents, the ^{1}H NMR spectrum can be recorded using a mixture of DMF-d_7 and carbon disulfide. Amino protons at positions 5 and 7 appear as deshielded broad singlets at 11.7 and 11.9 ppm, respectively (see Supplementary data). It is worth mentioning that the new compound **9** endowed with a uracil moiety is an appealing building block for the construction of a variety of supramolecular ensembles involving fullerene derivatives.

2.1. Dynamic ^{1}H NMR spectroscopy

The structure of the new cycloadducts was established on the basis of their spectroscopic data. The ^{13}C NMR spectra indicated that the cycloadduct molecule has an average C_s symmetry attributed to the fast flipping motion of the cyclohexene ring linking the pyrimidine ring to the C_{60} core. The methylene carbons (C3 and C10) appear between 39 and 47 ppm while the quaternary sp^3 carbon atoms of attachment to the cyclohexene ring (C1 and C2) resonate around 65 ppm. These chemical shift values confirm the 6,6-ring junction on the C_{60} cage. The ^{1}H NMR spectra show the methylene



Scheme 2. The two-step synthesis of cycloadduct **2** and alternative approaches to cycloadduct **3**.

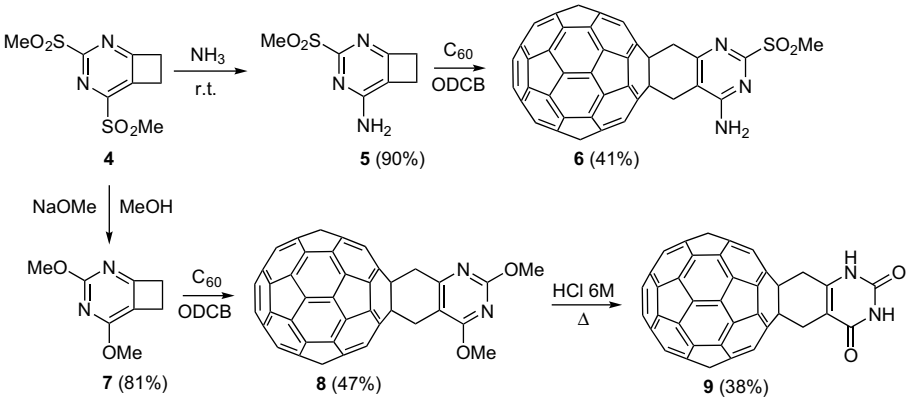


Scheme 3. Energy levels for the HOMO (diene) and LUMO (dienophile).

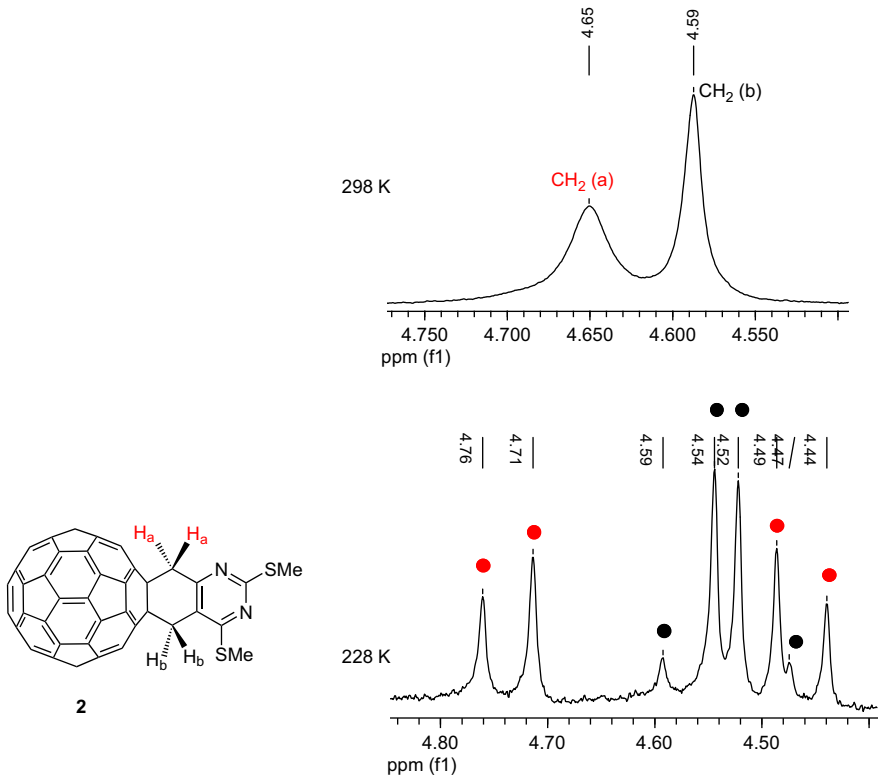
protons at C3 and C10 as two broad singlets at room temperature. At higher temperatures, these singlets sharpen indicating a dynamic process. This is attributed to a boat-to-boat cyclohexene ring interconversion, which was studied by variable temperature NMR (VT NMR). The coalescence temperature, and thus the $\Delta G^{\ddagger}$ value for this interconversion, depend on the nature of the heterocyclic ring (pyrazine or thiophene).[11] For the pyrimidine cycloadducts, these thermodynamic parameters are a function of the alkyl or aryl substitution on the pyrimidine ring.[18] Pyridine and benzene cycloadducts with a hydroxyl group attached to the cyclohexene ring adopt conformers with the OH group in pseudoaxial and pseudoequatorial position, respectively.[19]

The ^{1}H NMR spectrum of **2** at 298 K in a mixture of CS_2 and $CDCl_3$ shows two broad singlets at 4.65 $(CH_2)_a$ and 4.59 ppm $(CH_2)_b$, respectively (Scheme 5). These assignments were based on the smaller distance from $(CH_2)_a$ (in red) to the nearest nitrogen atom in the pyrimidine ring. At 228 K two overlapped AB systems can be observed and have the following calculated parameters: δ_A=4.71, δ_B=4.54, J=14.16 Hz for $(CH_2)_a$ and δ_A=4.52, δ_B=4.49, J=14.65 Hz for $(CH_2)_b$. The coalescence of $(CH_2)_a$ is observed at 258 K while the $(CH_2)_b$ protons coalesce at 261 K (see Supplementary data). Compound **8** exhibits a similar spectroscopic behaviour (Scheme 6), showing two broad singlets at 298 K centred at 6.05 $(CH_2)_a$ and 5.99 $(CH_2)_b$ ppm. Cooling to 228 K produces two overlapped AB systems from which were calculated chemical shifts and coupling constants of δ_A=6.15, δ_B=5.90, J=13.92 Hz for $(CH_2)_a$ and δ_A=6.14, δ_B=5.78, J=14.65 Hz for $(CH_2)_b$. Coalescences were at 254 K for $(CH_2)_a$ and 263 K for $(CH_2)_b$ (see Supplementary data). The calculated thermodynamic parameters for compounds **2** and **8** are collected in Table 1.

It is noteworthy that cycloadducts **2** and **8** have lower activation free energies for both methylene groups (a and b) than those determined for similar cycloadducts bearing methyl or aryl substituents on the pyrimidine ring.[18] However, the experimental values are in the range of those previously determined for six-membered heterocycles analogues[11] while values for pentagonal heterocycles are much higher.[12] These findings demonstrate a clear relationship



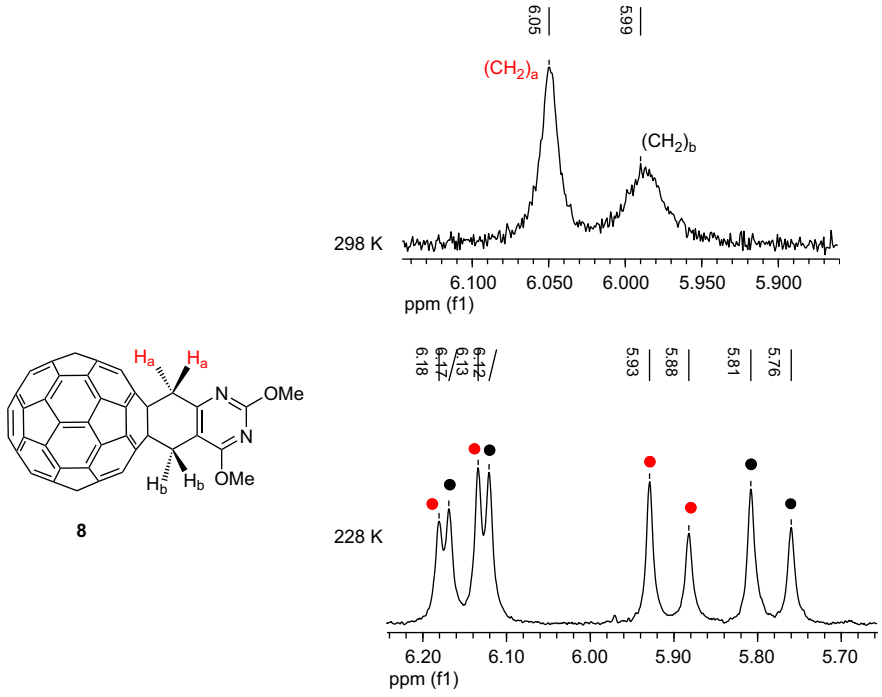
Scheme 4. Synthesis of aminomethylsulfonyl fullerene derivative **6**, dimethoxy cycloadduct **8**, and uracil derivative **9**.



Scheme 5. Temperature-dependent ^{1}H NMR spectra of compound **2**.

between activation free energy and the electronic character of the substituents attached at positions 2 and 4 of the pyrimidine moiety. Although these groups are not spatially close to the cyclohexene bridge, their electronic character plays an important role in the flipping motion of the cyclohexene ring. In contrast, VT NMR experiments on adducts having various aromatic rings other than pyrimidine showed that steric effects mainly influence the inversion rate of the cyclohexene ring.[21] MM2 calculations reveal that the cyclohexene ring in these polyaromatic cycloadducts adopts a half-boat as its most stable conformation.[21]

For cycloadduct **8**, the PM3 method predicts a boat as the lowest energy conformation for the cyclohexene (Fig. 1). At room



Scheme 6. Temperature-dependent ^{1}H NMR spectra of compound **8**.

Table 1
Activation of free energies determined for cycloadducts **2** and **8**

Compound	T_c (K)	$\Delta G^{\ddagger}$ (kJ mol^{-1})[a]	J_{AB} (Hz)	$\Delta G^{\ddagger}$ (kJ mol^{-1})[b]	δ (ppm)
2	258 (a)	61.7	14.16	59.2	a_1=4.71
	261 (b)	61.9	14.17	62.3	a_2=4.49
					b_1=4.54
					b_2=4.52
8	254 (a)	60.6	13.92	60.7	a_1=6.15
	263 (b)	68.0	14.65	68.2	a_2=5.90
					b_1=6.14
					b_2=5.78

[a] Activation free energies at the coalescence temperatures calculated according to $\Delta G^{\ddagger}=aT[9.972+\log(T+\Delta\nu)]$; $a=1.914\times10^{-2}$ kJ mol^{-1} (Ref. 20).
[b] Activation free energies at the coalescence temperatures calculated according to $\Delta G^{\ddagger}=aT[9.972+\log(T+(\delta\nu^2+6J_{AB}^2)^{1/2})]$; $a=1.914\times10^{-2}$ kJ mol^{-1} (Ref. 20).

temperature the cycloadducts have a C_s symmetry in the NMR spectra as a result of the rapid motion of the cyclohexene unit at room temperature. This boat conformation was also found in the case of alkyl- and arylsubstituted pyrimidine cycloadducts.[18]

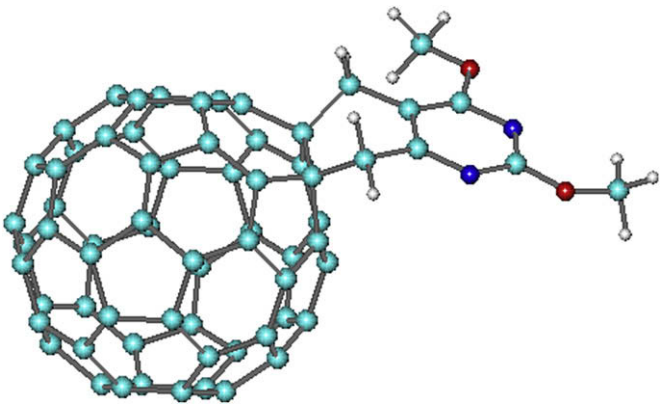


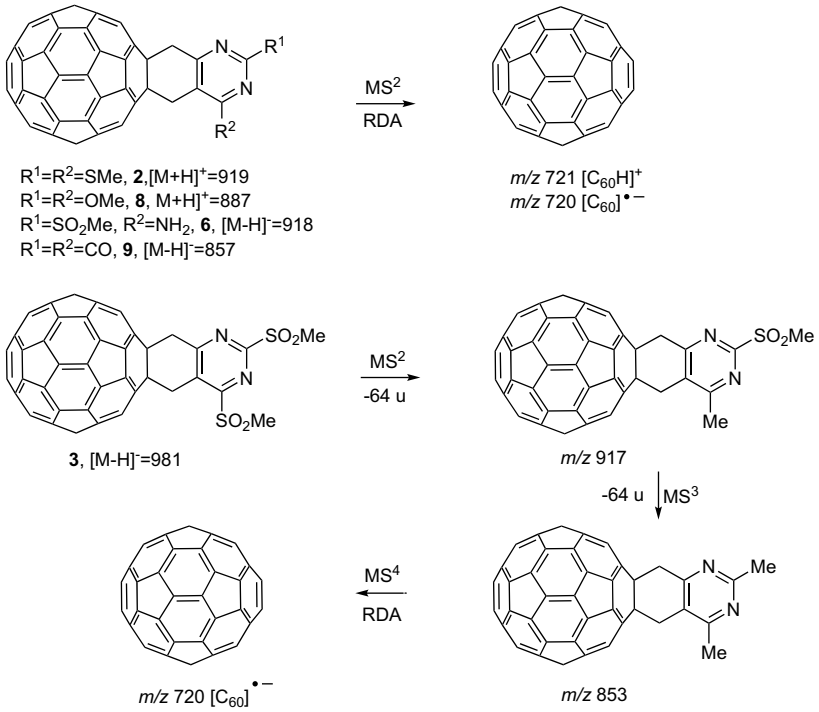
Figure 1. Minimum energy conformation of the PM3 optimized structure of cycloadduct **8**.

2.2. Mass spectra of cycloadducts

Mass spectrometry of fullerene cycloadducts is a powerful tool to investigate the gas-phase reactions of this class of compounds.[22] The electrochemical properties of fullerene derivatives permit the analysis of these molecules by electrospray ionization (ESI) mass spectrometry.[23] The well-known retro-Diels–Alder reaction (RDA) [24]can be originated in a mass spectrometer[25] and is one of the most investigated spectrometric process in the fullerene chemistry.[26] Thus, ESI-MS demonstrates that isoxazolino fullerene derivatives undergo retro-cycloaddition reaction with elimination of the corresponding 1,3-dipole molecule.[27] The FAB mass spectra of methyl- and arylsubstituted fulleropyrimidine cycloadducts show that the RDA reaction takes place easily forming as base peak the corresponding *m*/*z* 720 ion.[28] The ESI and APCI mass spectra (in positive as well negative mode of detection) of the reported **2**, **6**, **8**, and **9** exhibit a similar behaviour, where the MS^2 spectra reveal that the RDA process is the main fragmentation pattern. However, compound **3** extrudes consecutively two sulfur dioxide molecules (2×64 u) forming a dimethylated pyrimidine cycloadduct,[27] which finally undergoes the expected RDA elimination (Scheme 7). It is important to note that this is the first observation where an RDA reaction takes place not directly from the isolated molecular ion but from a prior double elimination of a small molecule.

3. Conclusion

In summary, we have carried out the synthesis of novel [60]fullerene cycloadducts bearing a pyrimidine ring endowed with substituents, which have been further transformed into different chemical functionalities. The dynamic behaviour of the new cycloadducts has been studied by VT ^{1}H NMR and the thermodynamic parameters determined for the flipping cyclohexene reveal the influence of the substituents on the coalescence process. Finally, the mass spectra of the cycloadducts confirm the retro-Diels–Alder process in a straightforward method or by following a double elimination process involving a small molecule. Work is in progress



Scheme 7. ESI mass spectra of new cycloadducts **2**, **3**, **6**, **8**, and **9**.

in order to determine the usefulness of some of the novel fullerene cycloadducts such as the uracil containing derivative as building blocks for the construction of further supramolecular architectures.

4. Experimental

4.1. General

Triflic anhydride was prepared from TfOH[29] and distilled twice over P_2O_5 before use. ^1H NMR and ^{13}C NMR for cyclobutapyrimidines were recorded in $CDCl_3$ and DMSO-d_6 at 300 (Bruker Avance 300) and 500 MHz (Bruker AM-500) and 57 and 125 MHz and referenced to 7.26 and 77.00 ppm for chloroform, 2.50 and 39.5 ppm for DMSO, respectively. NMR spectra of cycloadducts were recorded in mixtures of $CDCl_3/CS_2$ and DMF-d_7/CS_2. In this last case, spectra were referenced to 8.01 and 166.5 ppm for DMF. ^1H NMR of compound **6** was recorded in 1,1,2,2-tetrachloroethane-d_2 at 80 °C and referenced to 5.94 ppm. Homonuclear *J* couplings were confirmed by single-frequency experiments. Multiplicity assignments of ^{13}C NMR signals were made from DEPT spectra. Solid state NMR experiments were performed with a Bruker DSX 500 Wide Bore spectrometer (magnetic field strength 11.7467 T, resonate frequency of ^{13}C 125.75 MHz). Samples were packed in 4 mm zirconia rotors and spun at 9 KHz under magic angle using $p1$=5 μs and $p15$ (contact time)=5 ms. The chemical shifts were referenced to external carbonyl group of glycine at 176.1 ppm. VT NMR was carried out at 500 MHz using a methanol standard for the calibration of temperature. ESI and APCI mass spectra were recorded on a Bruker Esquire LC while HRMS were recorded using an FTMS Bruker APEX Q IV at 4.7 T under ESI conditions.

4.1.1. 2,4-Bis(methylsulfanyl)-5,6-dihydrocyclobuta[d]-pyrimidine (**1**)

Compound **1** was prepared from cyclobutanone, methythiocyanate, and triflic anhydride following reported synthetic methods[15b,16] in 42% yield, mp 102–103 °C (MeOH); IR (KBr) ν=1546, 1427, 1334 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ=2.51 (s, 3H, SMe), 2.53 (s, 3H, SMe), 3.10 (t, J=3.9 Hz, 2H, CH_2), 3.30 (t, J=3.9 Hz, 2H, CH_2); ^{13}C NMR (57 MHz, $CDCl_3$, 25 °C): δ=11.5 (SMe), 14.2 (SMe), 27.1 (CH_2), 35.0 (CH_2), 129.5, 136.5, 161.6, 170.2 (arom); MS (EI, 70 eV) *m/z* 198($M^{+\bullet}$, 198), 183 (M−CH_3, 72), 137 (183−SCH_2, 19), 78 (21). Anal. Calcd for $C_8H_{10}N_2S_2$: C, 48.45; H, 5.08; N, 14.13; S, 32.34. Found: C, 48.31; H, 4.89; N, 13.98; S, 32.14.

4.2. General procedures for the functionalization of cyclobutapyrimidines

4.2.1. 2,4-Bis(methylsulfonyl)-5,6-dihydrocyclobuta[d]-pyrimidine (**4**)

Compound **4** was prepared by oxidation from **1** according to previously reported method[15] in 88% yield, mp 185–186 °C (EtOH); IR (KBr) ν=1620, 1427, 1176, 1072 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ=3.21 (s, 3H, OMe), 3.27 (s, 3H, OMe), 3.56 (t, J=5 Hz, 2H, CH_2), 3.72 (t, J=5 Hz, 2H, CH_2); ^{13}C NMR (57 MHz, $CDCl_3$, 25 °C): δ=29.1 (CH_2), 38.3 (SO_2Me), 39.4 (CH_2), 39.6 (SO_2Me), 139.3, 156.2, 160.2, 181.3 (arom.); MS (ESI) *m/z* 263 $[M+H]^+$. Anal. Calcd for $C_8H_{10}N_2O_4S_2$: C, 36.63; H, 3.84; N, 10.68; S, 24.45. Found: C, 36.50; H, 3.90; N, 10.53; S, 24.11.

4.2.2. 4-Amino-2-(methylsulfonyl)-5,6-dihydrocyclobuta[d]pyrimidine (**5**)

Compound **5** was prepared from **4** according to previously reported methods[15] in 89% yield, mp 183–184 °C (EtOH); IR (KBr) ν=3495, 3300, 3120, 1404, 1190, 1010 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 25 °C): δ=2.95 (t, J=3.9 Hz, 2H, CH_2), 3.09 (s, 3H, SO_2Me), 3.19 (t, J=3.9 Hz, 2H, CH_2), 3.23 (s, 3H, SO_2Me), 3.87 (br s, 2H, NH_2); ^{13}C NMR (57 MHz, DMSO-d_6, 25 °C): δ=26.5 (CH_2), 34.0 (CH_2), 38.8 (SO_2Me), 121.0, 156.6, 157.4, 170.1; MS (EI, 70 eV) *m/z* (%B) 199 ($M^{+\bullet}$, 27), 184 (M−CH_3, 65), 120 (M−SO_2Me, 56), 42 (100). Anal. Calcd for $C_7H_9N_3O_2S$: C, 42.20; H, 4.55; N, 21.09; S, 16.09. Found: C, 41.90; H, 4.33; N, 20.89; S, 15.87.

4.2.3. 2,4-Dimethoxy-5,6-dihydrocyclobuta[d]pyrimidine (**7**)

Compound **7** was prepared from **4** according to previously reported methods[15] in 81% yield, mp 46–47 °C (MeOH); IR (KBr) ν=1211, 1085 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ=3.03 (t, J=4 Hz, 2H, CH_2), 3.24 (t, J=4 Hz, 2H, CH_2), 3.93 (s, 6H, OMe); ^{13}C NMR (57 MHz, $CDCl_3$, 25 °C): δ=25.5 (CH_2), 34.6 (CH_2), 53.8 (OMe), 54.7 (OMe), 113.9, 163.5, 166.0, 175.2 (arom); MS (ESI) *m/z* 189 $[M+Na]^+$, 166 $[M+H]^+$. Anal. Calcd for $C_8H_{10}N_2O_2$: C, 57.82; H, 6.07; N, 16.86. Found: C, 57.57; H, 5.88; N, 16.58.

4.3. Synthesis of Diels–Alder cycloadducts: general procedure

A solution of the appropriate cyclobutapyrimidine (1 mmol) and C_{60} (1 mmol) in *o*-dichlorobenzene (20 mL) was heated under reflux (180 °C) for 48 h. The progress of the reaction was monitored by TLC. Some part of the solvent was removed under reduced pressure and the residue was fractionated by column chromatography using first as eluent carbon disulfide to eliminate the rest of solvent and the C_{60} not transformed. A mixture of eluents (hexane/ethyl acetate 8/2) permits to obtain the corresponding cycloadducts.

4.3.1. 1′,2′,3′,4′-Tetrahydro-6′,8′-bis(methylsulfanyl)quinazolino-[2′,3′:1,2][60]fullerene (**2**)

Following the general procedure, the reaction of **1** with C_{60} affords the compound in 40% yield. IR (KBr) ν=2921, 1535, 1338, 858 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3/CS_2$, 25 °C): δ=2.75 (s, 3H, SMe), 2.77 (s, 3H, SMe), 4.58 (br s, 2H, CH_2), 4.65 (br s, 2H, CH_2); ^{13}C NMR (57 MHz, $CDCl_3/CS_2$, 25 °C): δ=12.7 (SMe), 14.8 (SMe), 39.7 (CH_2), 45.9 (CH_2), 64.3 ($Csp^3$of C_{60}), 64.7 (Csp_3 of C_{60}), 122.9, 140.8, 142.2, 142.3, 142.5, 142.6, 142.7, 145.5, 145.6, 145.9, 146.1, 146.2, 146.3, 146.7, 146.8, 147.0, 148.2, 155.7, 155.9, 163.9, 167.4, 171.9; ^{13}C NMR (CP-MAS): δ=13.5(SMe), 19.4 (SMe), 32.9 (CH_2), 40.9 (CH_2), 65.1 ($Csp^3$of C_{60}), 123.8, 135.8, 140.1, 141.7, 142.5, 145.5, 155.9, 163.7, 166.2, 172.0; MS (ESI) *m/z* 919 $[M+H]^+$; HRMS calculated for $[M+H]^+$ $C_{68}H_{11}N_2S_2$: 919.03638, found: 919.04003.

4.3.2. 1′,2′,3′,4′-Tetrahydro-6′,8′-bis(methylsulfonyl)quinazolino-[2′,3′:1,2][60]fullerene (**3**)

Following the general procedure, the reaction of **4** with C_{60} affords the compound in 19% yield. Compound **3** can also be prepared (90% yield) by reaction of cycloadduct **2** with *m*-CPBA in dichloromethane following the same procedure used to obtain **4**. The low solubility avoids to record the NMR spectra in liquid phase. ^{13}C NMR (CP-MAS): δ=32.9 (SO_2Me), 41.2 (SO_2Me), 42.5 (CH_2), 46.9 (CH_2), 63.8 ($Csp^3$of C_{60}), 131.0, 136.7, 142.5, 145.5, 155.3, 161.6, 175.2; MS (APCI) *m/z* 982, $[M^{\bullet-}]$; HRMS calculated for $C_{68}H_{10}N_2O_4S_2$: 982.00824, found: 982.01055.

4.3.3. 1′,2′,3′,4′-Tetrahydro-6′-methylsulfonyl-8′-aminoquinazolino[2′,3′:1,2][60]fullerene (**6**)

Following the general procedure, the reaction of **5** with C_{60} affords the compound in 41% yield. IR (KBr) ν=3139, 1635, 1429, 1205, 1051, 785 cm^{-1}; ^1H NMR (300 MHz, 1,1,2,2-tetrachloroethane-d_2, 80 °C) δ=2.92 (br s, 2H, CH_2), 3.09 (br s, 2H, CH_2), 3.53 (s, 3H, SO_2Me), 8.19 (br s, 2H, NH_2); ^{13}C NMR (CP-MAS): δ=29.5 (SO_2Me), 40.3 (CH_2), 71.4 ($Csp^3$of C_{60}), 82.9 ($Csp^3$of C_{60}), 136.5, 141.3, 143.4, 148.8, 164.4; MS (ESI) *m/z* 918 $[M-H]^-$; HRMS calculated for $[MH]^-$ $C_{67}H_8N_3O_2S$: 918.03369, found: 918.03998.

4.3.4. 1′,2′,3′,4′-Tetrahydro-6′,8′-dimethoxyquinazolino-[2′,3′:1,2][60]fullerene (**8**)

Following the general procedure, the reaction of **7** with C_{60} affords the compound in 44% yield. IR (KBr) ν=2921, 1579, 1453, 1375, 1074, 727 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3/CS_2$, 25 °C): δ=4.13 (s, 3H, OMe), 4.14 (s, 3H, OMe), 4.55 (br s, 2H, CH_2), 4.61 (br s, 2H, CH_2); ^{13}C NMR (57 MHz, $CDCl_3/CS_2$, 25 °C): δ=46.1 (OMe), 46.2 (OMe), 54.1 (CH_2), 54.7 (CH_2), 64.8 ($Csp^3$of C_{60}), 65.0 (Csp_3 of C_{60}), 109.6, 133.3, 140.0, 141.4, 141.9, 142.0, 142.4, 142.9, 144.4, 144.5, 144.9, 145.1, 146.3, 147.5, 155.7, 164.4, 167,6, 168.1; MS (ESI) *m*/*z* 887 $[M+H]^+$; HRMS calculated for $[M+H]^+$ $C_{68}H_{11}N_2O_2$: 887.08203; found: 887.08522.

4.3.5. 1′,2′,3′,4′-Tetrahydroquinazolino[2′,3′:1,2][60]fullerene-6′,8′(5H-7H)-dione (**9**)

Cycloadduct **8** (88 mg, 0.1 mmol) is suspended in aqueous 6 M HCl and heated for 6 h. The solvent was removed at reduced pressure and the residue washed with water and methanol. The uracil **9** was obtained in 38% yield. IR (KBr) ν=3423, 3200, 1681, 1460, 1375, 1120, 769 cm^{-1}; ^1H NMR (300 MHz, DMF-d_7/CS_2, 25 °C): δ=4.70 (br s, 2H, CH_2), 4.95 (br s, 2H, CH_2), 11.68 (br s, 1H, NH), 11.89 (br s, 1H, NH); ^{13}C NMR (57 MHz, DMF/CS_2, 25 °C): δ=40.9 (CH_2), 41.4 (CH_2), 65.7 ($Csp^3$of C_{60}), 66.8 (Csp_3 of C_{60}), 107.7, 135.8, 136.3, 140.3, 140.4, 141.4, 141.9, 142.3, 142.5, 142.7, 142.8, 143.4, 144.9, 145.0, 145.6, 145.7, 145.8, 145.9, 146.1, 146.5, 146.7, 146.8, 147.9, 148.0, 151.9, 152.8, 156.5; MS (ESI) *m*/*z* 857 $[M-H]^-$; HRMS calculated for $[M-H]^-$ $C_{66}H_5N_2O_2$: 857.03510; found: 857.02997.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.05.026.

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