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Tether-Directed Selective Synthesis of Fulleropyrrolidine Bisadducts

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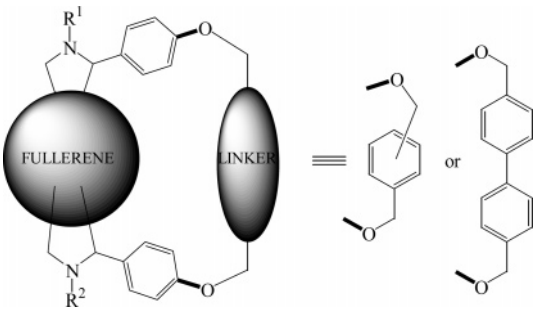

Selective synthesis of C_{60} bisadducts has been achieved by using the Prato 1,3-dipolar cycloaddition of tethered bis-azomethine ylides. New bis(benzaldehydes) **1**−**4** tethered by a rigid linker were prepared and used to direct the second cycloaddition of azomethine ylide to C_{60}. Equatorial, trans-4, trans-3, trans-2, and trans-1 bisadducts have been selectively prepared with this approach. However, the introduction of chiral centers in the pyrrolidine rings in the course of the reaction complicated the chemistry, as a number of stereoisomers theoretically could be formed. The structure determination of the isomeric bisadducts was made based on spectroscopic data and theoretical calculations. To our best knowledge, this represents the first example of a systematic study on tether-directed selective synthesis of C_{60} fulleropyrrolidine bisadducts.

Introduction

Bis-functionalized fullerenes have been widely used in biological studies, molecular devices, and advanced materials, due to their defined three-dimensional structures containing a variety of functional groups.[1−3] Tether-controlled bis-functionalization is critical to improve the yield of specific bisadduct isomers and to avoid tedious chromatographic separations.[1,2,4] Reviews on the diversity of methods for tether-directed multiple functionalization of C_{60} have appeared, which pointed out that each fullerene reaction, such as the Bingel−Hirsch reaction, the Diels−Alder reaction, or the Prato reaction, requires a specific design of tethers.[1a,4] In particular, tether-controlled bisadditions of malonates to C_{60} have been extensively studied.

Azomethine ylide [3+2] cycloaddition to C_{60} (the Prato reaction) has been proven to be a very efficient and facile functionalization method to prepare C_{60} derivatives for various applications.[5] The stepwise bisadditions of 1,3-dipolar azomethine ylides to C_{60} have been systematically studied, which lead to eight isomeric bisadducts when symmetric azomethine ylides are employed.[6,7] The structural assignment of C_{60} fulleropyrrolidine bisadducts has been accomplished by means of UV−vis, NMR, and transient EPR spectroscopy.[6−9] Each bisadduct shows unique absorption in the region of 400 to 750 nm and it

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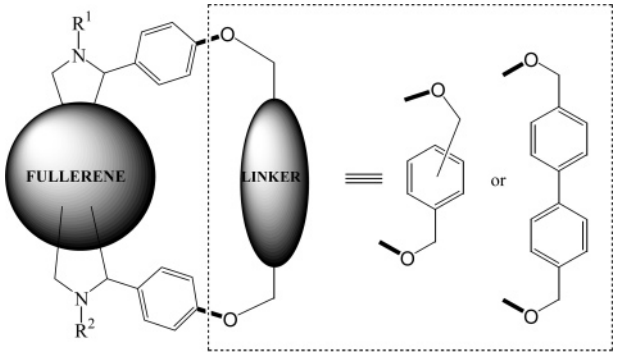
SCHEME 1. Schematic Representation of a New Tether-Directed Approach

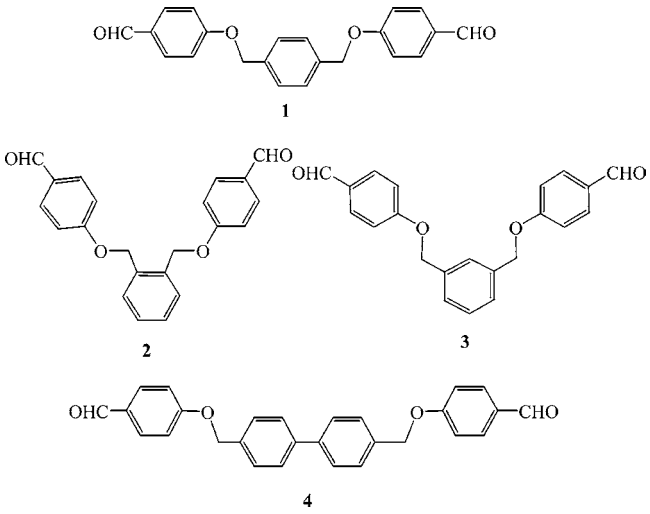


was widely used to determine the bisaddition patterns.[6] However, tether-controlled selective synthesis of fulleropyrrolidine bisadducts via the Prato reaction has not been studied until the recent report of D'Souza and co-workers on synthesis of Prato bisadducts with a dibenzo-18-crown-6 bisaldehyde as the tether. The D'Souza approach led to a bisadduct mixture containing several isomers that was directly used for further studies without separation.[10] Previously, Prato reported tether-assisted double [3+2] cycloadditions resulting in the formation of one pyrrolidine ring and one isoxazoline ring on C_{60} mainly with a cis-1 positional relationship.[11] Nakamura and co-workers also reported one example of tether-controlled double [3+2] cycloadditions to C_{60} leading to two cyclopentene rings attached on the C_{60} cage.[12] Very recently, Martin and co-workers reported a regioselective synthesis of cis-1 bisadducts resulting in one pyrrolidine ring and one cyclopentenone ring attached on the fullerene surface, through an intramolecular Pauson−Khand reaction starting with a fulleropyrrolidine monoadduct containing a terminal alkyne moiety.[13]

Results and Discussion

Design and Synthesis of Tethered Bisbenzaldehydes. In the present study, we demonstrate a novel approach for tether-controlled selective bisaddition of azomethine ylides to C_{60} and report the design of new tethers, together with the synthesis and structural characterization of several isomeric fulleropyrrolidine bisadducts. The basic problem was to find a readily preparable linker to connect the two pyrrolidine rings at the α-carbon atoms. Considering the formation mechanism of azomethine ylides and the dimensions of C_{60}, we began with a benzene ring attached on the α-carbon of the pyrrolidine rings to build the entire tether. Then a rigid linker (phenyl or biphenyl) was needed to link the two benzene rings (Scheme 1). However, the unavoidable introduction of chiral centers in the heterocycles in the course of the reaction complicated the chemistry, as a number of stereoisomers theoretically could be formed. The use of phenyl benzylic ether moiety also gives the possibility to cleave the linker, resulting in two phenols attached on the pyrrolidine rings.

SCHEME 2. Tethered Bis(benzaldehydes) 1−4



Bisaldehydes **1**, **2**, **3**, and **4** were prepared through the alkylation of *p*-hydroxybenzaldehyde by α,α′-dibromo *p*-xylene, α,α′-dibromo *o*-xylene, α,α′-dibromo *m*-xylene, and 4,4′-bis(bromomethyl) biphenyl, respectively (Scheme 2). The alkylation reaction was done at 80−90 °C in dry DMF in the presence of K_2CO_3. In most cases, pure products were obtained by filtration after a small amount of water was added to the reaction mixture. If needed, column chromatography (silica, CH_2Cl_2/EA, 95/5) was used to further purify the products. The typical yield of this reaction was about 75−82%. All compounds were characterized by ^1H and ^{13}C NMR and MS.

Selective Bisaddition of Azomethine Ylides Derived from Xylene-Tethered Bisbenzaldehydes to C_{60}. In a typical reaction, C_{60} was reacted with sarcosine and bisaldehyde **1** in a ratio of 1:4:1 for 4 h in refluxing ODCB. The reaction mixture was then subjected to a flash column (silica, 3 × 30 cm^2, toluene/hexanes 80:20 as eluant) and three bisadduct isomers **5**, **6**, and **7** were isolated in the ratio of 80:12:8. The overall yield of bisadducts was 70%. It should be noted that no preparative HPLC was required for further purification. All three isomers were characterized by UV−vis absorption spectroscopy, MALDI-MS, ^1H NMR, ^{13}C NMR, and 2D NMR. As stated earlier, UV−vis absorption spectroscopy is a routine and reliable tool to determine the bisaddition patterns of C_{60} bisadducts.[6] Herein, we assigned the bisaddition patterns of compound **5**−**7** by comparison of their UV−vis spectra with those of known C_{60} fulleropyrrolidine bisadducts.[6,7] Both isomers **5** and **6** showed the characteristic absorption of trans-3 fulleropyrrolidine bisadducts in the fingerprint region of 400 to 750 nm, and the UV−vis spectrum of isomer **7** is identical with that of a known equatorial fulleropyrrolidine bisadduct (see Figure 1).[6] For a C_{60} bisadduct prepared using our approach, the connectivity of the tether linkage[14] between the two pyrrolidine rings is another problem to be solved in addition to the bisaddition pattern. The structure determination of the tether linkage is complicated by

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(14) The nature of the tether linkage between the two pyrrolidine rings is complicated by two factors: (1) the tether (−phenyl−OCH_2−xylene/biphenyl−CH_2O−phenyl−) could be bound to either of the two α-carbon atoms of each pyrrolidine ring, which gives four combinations, and (2) the tertiary carbons to which the tether is attached are chiral. Thus, there could be as many as 16 theoretically possible tether linkages between the two pyrrolidine rings, depending on the symmetry of the bisaddition pattern. Numerous attempts to obtain crystals of bisadducts isomers suitable for X-ray crystallographic analysis failed.

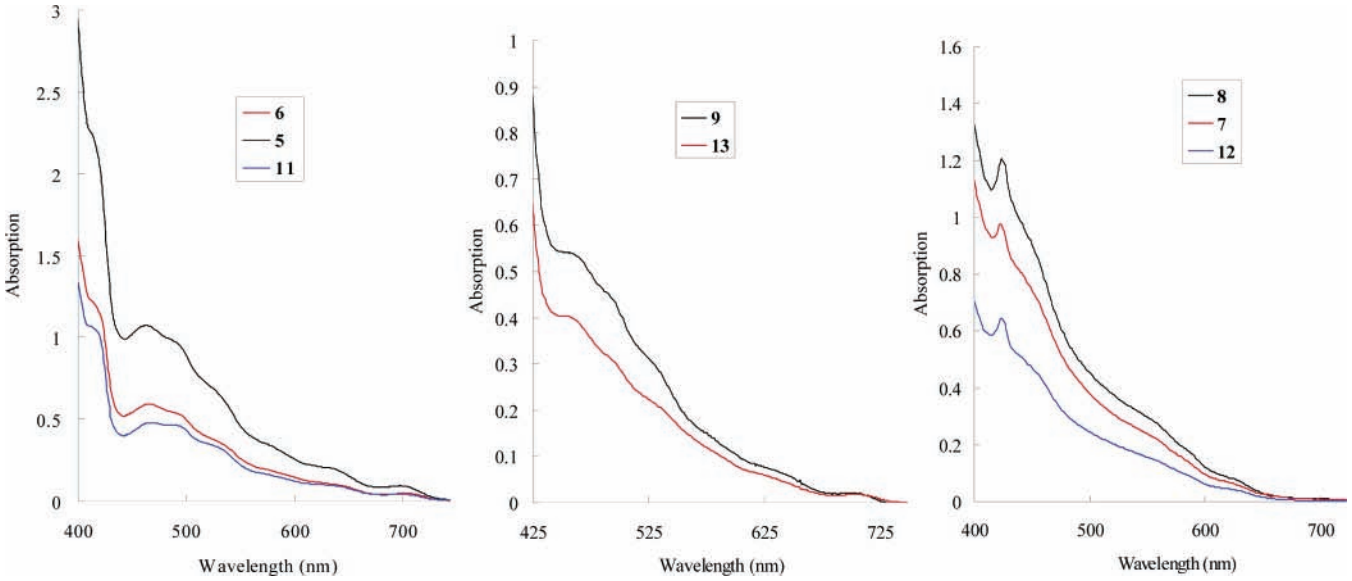

FIGURE 1. UV−vis absorption spectra of equatorial bisadducts **7**, **8** and **12**, trans-3 bisadducts **5**, **6**, and **11**, and trans-4 bisadducts **9** and **13**.

both the introduction of two stereogenic centers and the existence of a total of four α-carbon atoms in the two pyrrolidine rings, which gives a number of possible ways to link the two pyrrolidine rings.[14] However, with the aid of theoretical calculations, assignment of the structures of the bisadducts could be made from the spectral data.

The ^{1}H and ^{13}C NMR data clearly show that isomer **6** is C_2 symmetric, and isomers **5** and **7** are C_1 symmetric. The C_2 symmetry of compound **6** also matches the symmetry of the trans-3 bisaddition pattern. The ^{1}H NMR spectrum of bisadduct **6** has one singlet methyl peak, two doublet peaks for the pyrrolidine methylene protons, two doublet benzylic proton peaks, and one singlet peak for the pyrrolidine methine proton. Due to the chiral environment, the two protons of the pyrrolidine methylene are diastereotopic and similarly the two benzylic protons are also diastereotopic.[15] In its ^{13}C NMR spectrum, there are 37 sp^2 carbon signals, including 28 fullerene-based sp^2 carbon signals and 6 sp^3 carbon peaks. The proton and carbon NMR spectra of bisadducts **5** and **7** show twice the corresponding peaks of compound **6**. COSY spectra of bisadduct isomers helped assign the diastereotopic pairs, as shown in Figure 2 (COSY spectrum of bisadduct **5** with C_1 symmetry, showing the aliphatic region except for the two methyl peaks). Thus, the two singlet peaks at 4.14 and 4.41 ppm are from the two methine protons of the pyrrolidine rings. There are eight doublet methylene proton peaks, which can be seen as four diastereotopic pairs. Peaks at 3.82 and 4.86, 4.08 and 4.78 ppm are assigned to the benzylic methylene protons, and peaks at 4.83 and 5.22, 4.94 and 5.04 ppm are assigned to the methylene protons of the pyrrolidine rings by comparison of their chemical shifts and *J*-coupling constants with those of several fulleropyrrolidine monoadducts having similar structures.[15]

AM1 molecular modeling was used to assist in establishing the isomeric structures of three bisadducts, as a number of reports have used theoretical calculations for structure determination of C_{60} bisadducts.[16] Out of all the possible isomers of trans-3 bisadducts, only two of them have relatively low heats

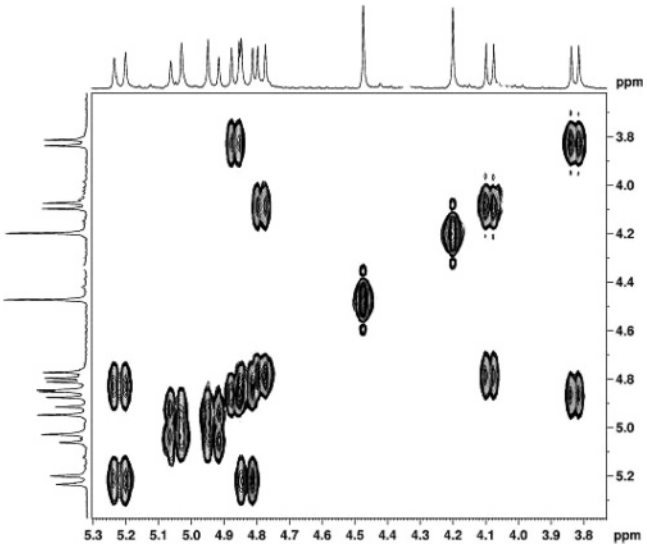

FIGURE 2. COSY spectrum of bisadduct **5** showing aliphatic protons except for the two methyl groups.

of formation as shown in Scheme 3. The AM1 heats of formation of compounds **5** and **6** are 1233.4 and 1235.1 kcal/mol, respectively. The C_1-symmetric trans-3 bisadduct **5** has lower energy than the C_2-symmetric trans-3 bisadduct **6** by 1.7 kcal/mol.[17] This is consistent with the experimental data that the major trans-3 isomer has no symmetry and the minor trans-3 isomer has C_2 symmetry, as demonstrated by their ^{1}H and ^{13}C

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(17) See Supporting Information for the AM1 energy calculation of all bisadduct isomers with use of the Spartan 04 by Wavefunction. Given the endothermicity of the present reaction, this thermodynamic argument can be readily transformed into a kinetic one by virtue of the Hammond postulate.

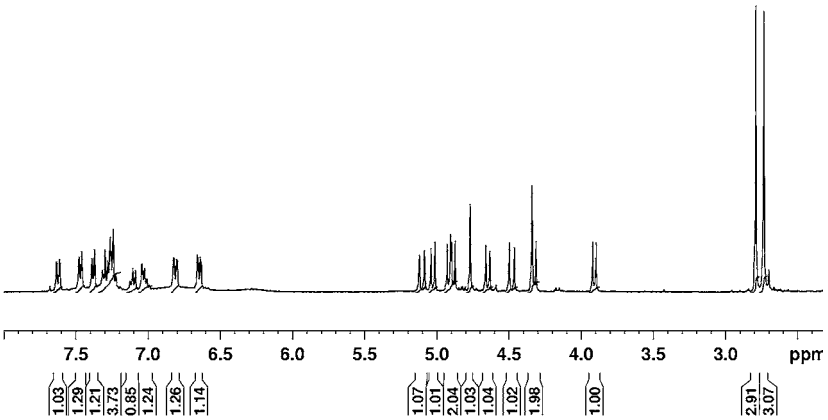
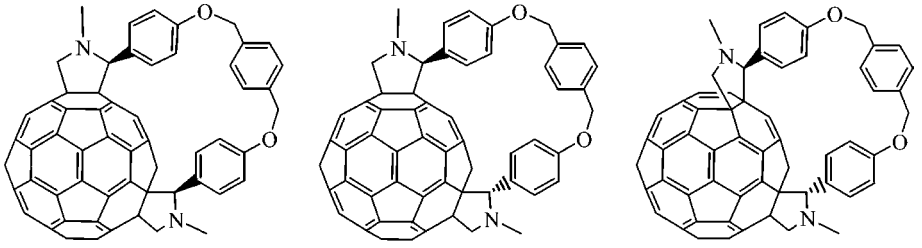


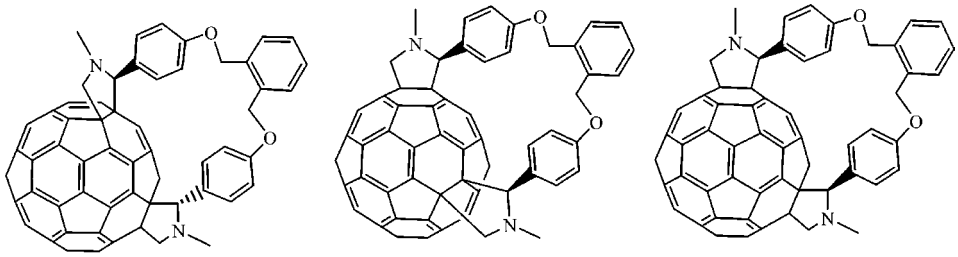
FIGURE 3. ^{1}H NMR spectrum of bisadduct **10**.

SCHEME 3. Fulleropyrrolidine Bisadducts Obtained from Bisaldehyde 1



trans-3 **5** *trans-3* **6** *equatorial* **7**

SCHEME 4. Fulleropyrrolidine Bisadducts Obtained from Bisaldehyde 2



equatorial **8** *trans*-4 **9** *trans-3* **10**

NMR spectra. On the basis of theoretical calculations and spectroscopic data, the structures of bisadducts **5** and **6** were assigned as shown in Scheme 3.

Similar theoretical calculations showed that there is only one compound having significantly lower AM1 heats of formation of 1236.5 kcal/mol among all of the possible equatorial bisadduct isomers.[17] The equatorial bisadduct is apparently nonsymmetric as depicted by its NMR data because two chiral centers were introduced in the pyrrolidine rings. Thus, the structure of the bisadduct **7** was assigned as shown in Scheme 3. Each structure in Scheme 3 represents a racemate. In summary, bisaddition of azomethine ylides derived from bisaldehyde **1** and sarcosine to C_{60} selectively led to the formation of three bisadduct isomers with two bisaddition patterns, with 92% selectivity for trans-3 bisadducts.

Reaction of bisaldehyde **2** with C_{60} and sarcosine in a ratio of 1:1:4 in refluxing ODCB yielded three isomeric bisadducts **8**, **9**, and **10**, with relative yields of 80%:15%:5% (Scheme 4). Three compounds were isolated in pure form by using flash column chromatography (silica, toluene/hexanes 80:20). Their bisaddition patterns were assigned by comparison of their UV−vis absorption spectra with those of known equatorial, trans-4, and trans-3 bisadducts, respectively (Figure 1).[6,7] All three compounds were characterized by means of MALDI-MS, ^{1}H NMR, ^{13}C NMR, and 2D NMR as well. The equatorial bisadduct **8** and trans-3 bisadduct **10** have no symmetry elements according to their NMR spectra, while bisadduct **9** is C_s symmetric, matching the symmetry of the trans-4 bisaddition pattern. There are 39 sp^2 carbon signals (30 of which are fullerene-based carbon peaks) and 6 sp^3 carbon signals in the ^{13}C NMR spectrum of compound **9**. Due to the presence of chiral centers, the protons of the methylene groups ($-N-CH_2-$ and $-O-CH_2-$) are diastereotopic as is clearly shown in the proton NMR spectrum of compound **10** (Figure 3). In a manner similar to bisadducts **5**−**7**, the tether linkages of bisadducts **8**−**10** were assigned on the basis of spectroscopic data with the aid of theoretical calculations (see the Supporting Information). The heats of formation of equatorial bisadduct **8** are 1234.8

TABLE 1. Bisaddition of Tethered Azomethine Ylides to C_{60}

bis(benzaldehydes)	bisadducts (rel ratio)	bisaddition patterns	symmetry
1	**5** (80%)	trans-3	C_1
(*p*-xylene-tethered)	**6** (12%)	trans-3	C_2
	7 (8%)	equatorial	C_1
2	**8** (80%)	equatorial	C_1
(*o*-xylene-tethered)	**9** (15%)	trans-4	C_s
	10 (5%)	trans-3	C_1
3	**11** (5%)	trans-3	C_2
(*m*-xylene-tethered)	**12** (35%)	equatorial	C_1
	13 (60%)	trans-4	C_1

kcal/mol, which is 8.1 kcal/mol lower than that of the second lowest energy structure.[17] The calculated structure with the lowest heats of formation among all possible trans-4 bisadduct isomers is C_s symmetric, which matches the NMR data of the isolated trans-4 bisadduct (Scheme 4).[17]

When bisaldehyde **3** was reacted with C_{60} and sarcosine in refluxing ODCB, three bisadduct isomers were also isolated in an overall yield of 68%. Bisadducts **11**, **12**, and **13** showed the characteristic absorption of trans-3, equatorial, and trans-4 bisadducts, respectively (Figure 1).[6,7] The relative yield of the three bisadducts **11**, **12**, and **13** was 5:35:60, which was different from the ratio of the three bisadducts (trans-3, equatorial, and trans-4) formed from the double Prato reaction using *o*-xylene tethered bisaldehyde **2** where the equatorial isomer is the only major product. All three isomers were characterized by absorption spectroscopy, MALDI-MS, ^{1}H NMR, ^{13}C NMR, and 2D NMR. In a similar manner, the tether linkages of bisadducts **11**−**13** were assigned on the basis of spectroscopic data with the aid of theoretical calculations (see Scheme 5 and the Supporting Information for AM1 energy calculation).

Table 1 summarizes the results of bisadditions of tethered azomethine ylides derived from bis(aldehydes) **1**−**3** to C_{60}, together with their relative yields and isomeric structures assigned from spectral data and calculations. Bisaddition of *p*-xylene tethered azomethine ylides to C_{60} mainly formed trans-3 bisadducts with a selectivity of 92%, and bisaddition of *o*-xylene tethered azomethine ylides to C_{60} mainly gave equatorial bisadducts with 80% selectivity, while both trans-4 and equatorial bisadducts could be formed in the ratio of 60:35 when *m*-xylene tethered bis(benzaldehydes) was used. The difference in bisaddition selectivity in these three cases can be explained by the varying distance and geometry of the two azomethine ylides due to the isomeric xylene tethers.

Selective Bisaddition of Azomethine Ylides Derived from Biphenyl-Tethered Bisbenzaldehydes to C_{60}. Among the eight geometrical bisadduct isomers isolated from the sequential additions of 2 equiv of azomethine ylides, the trans-1 compound is almost always the least abundant one.[6,7] Therefore, it is necessary to develop a tether-directed approach to give access to various trans-1 fulleropyrrolidine bisadducts. It has been shown to be very difficult to develop extended tethers with suitable length and conformation that could span the entire C_{60} cage and direct the second addition onto the trans-1 and even trans-2 positions, when tether-directed synthesis of C_{60} bisadducts through cyclopropanation reactions was studied.[18] Here we extended our study to a longer spacer, biphenyl-tethered bis(benzaldehyde)s, in order to prepare trans-2 and trans-1 bisadducts. In a manner similar to the above-described procedures, bisaldehyde **4** was reacted with C_{60} and sarcosine (1:1:4) to prepare bisadducts in refluxing ODCB (Scheme 6).

Two bisadduct isomers and a small amount of monoadduct were isolated by using flash chromatography (silica, 3 × 30 cm^2, toluene/hexanes 90:10 as eluant) and characterized by MALDI-MS, NMR, and UV−vis. The overall yield of the two bisadducts was 68%, and the ratio between compounds **14** and **15** was 2:3. Bisadduct **14** showed the unique absorption spectrum of a trans-1 bisadduct, with two major absorption peaks at 460 and 491 nm.[6,7] The UV−vis spectrum of bisadduct **15** is identical with that of a known trans-2 fulleropyrrolidine bisadduct in the fingerprint region of 400 to 750 nm, with four main peaks at 433, 479, 656, and 725 nm.[6,7] Therefore, the two bisadducts were assigned as trans-1 and trans-2 isomers. Because of the introduction of two chiral centers in the pyrrolidine rings and the presence of a biphenyl moiety, neither bisadduct is symmetric. This was evident from their NMR data, which show two methyl peaks, two singlet methine peaks, four doublet benzylic proton peaks, and four doublet pyrrolidine methylene peaks (AB quartet) for each compound. Theoretical calculations were conducted to help assign the topology of the tether linkage for both of the trans-2 and trans-1 bisadducts. The calculations revealed that one out of the four possible trans-1 isomers shown in Scheme 6 has a significantly lower heat of formation, 1255.4 kcal/mol, which is 12.3 kcal/mol lower than that of the second lowest energy structure. As far as the trans-2 bisadducts are concerned, 16 possible isomers were optimized, revealing that the structure shown in Scheme 6 has the lowest heat of formation, 1253.2 kcal/mol. On the basis of both the spectroscopic data and theoretical calculations, the two bisadducts isolated from the double [3+2] cycloaddition of azomethine ylides derived from bis(benzaldehyde) **4** are assigned as shown in Scheme 6.

Monoaddition of Tethered Azomethine Ylides to C_{60}. Monoaddition of azomethine ylides derived from bis(benzaldehydes) **1**−**4** and sarcosine to C_{60} was also studied. A 1:1:1 mixture of bis(benzaldehyde), sarcosine, and C_{60} was refluxed in toluene for 4 h and the corresponding monoadduct was virtually the only separable product, purified by silica flash chromatography (Scheme 7). The typical yield was around 70%. Monoadducts **16**−**19** prepared from compounds **1**−**4**, respectively, were characterized by MALDI-MS, ^{1}H NMR, ^{13}C NMR, and UV−vis. For instance, a proton peak at 9.79 ppm and a sp^2 carbon signal at 189.2 ppm corresponding to aldehyde functionality are present in the NMR spectra of monoadduct **18**. Interestingly, the monoadduct was still the only major product even when a large excess of sarcosine was used in this reaction in refluxing toluene. However, at elevated temperature, such as in refluxing chlorobenzene or ODCB, bisadducts were formed and only trace amounts of monoadduct could be detected. In fact, the same reactivity was observed for all four bisaldehydes. This temperature effect could be used to control the bisadditions of two different azomethine ylides (from two different amino acids) to C_{60}. This is important when two different groups are attached to the two pyrrolidine nitrogen atoms.

Potential Applications of Fullerene Bisadducts Prepared by the Current Approach. C_{60} is a 3D molecular platform, which can anchor two, three, or even more building blocks, such as pyridine and polypyridine coordination ligands, on the

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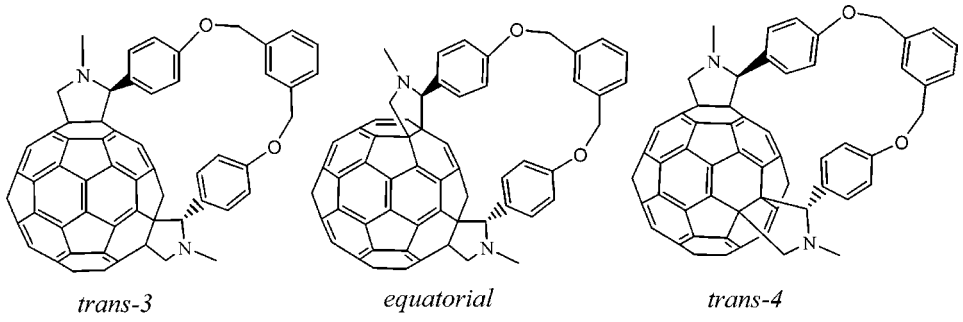
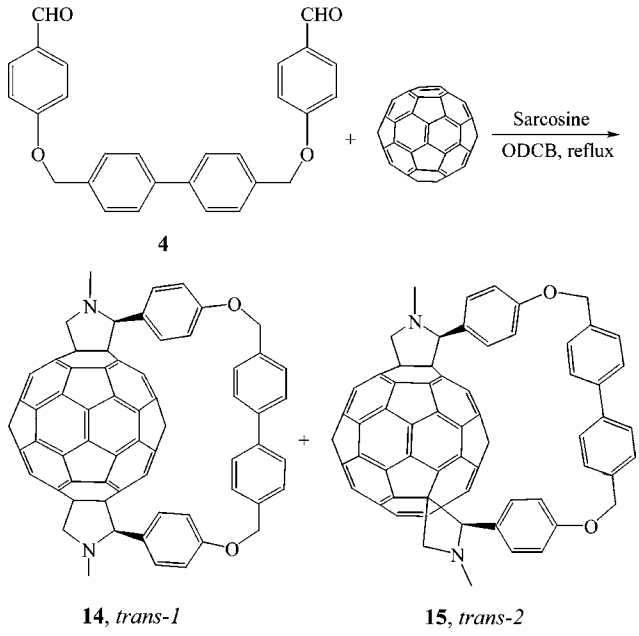
SCHEME 5. Fulleropyrrolidine Bisadducts Obtained from Bisaldehyde 3



trans-3 **11** *equatorial* **12** *trans-4* **13**

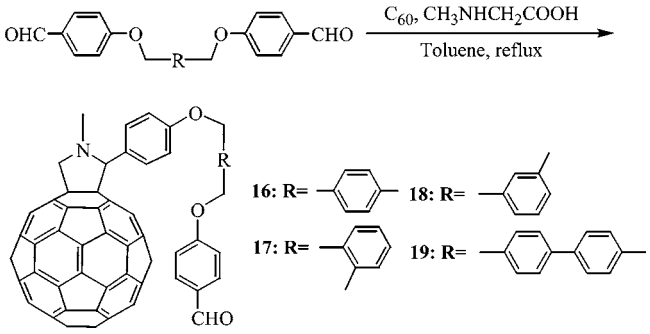
SCHEME 6. Tether-Directed Synthesis of Trans-1 and Trans-2 Bisadducts



4

14, *trans-1* **15**, *trans-2*

SCHEME 7. Monoaddition of Bis(aldehydes) 1−4 to C_{60}



cage surface with defined geometry.[19,20] Coordination of such building blocks to transition metals could lead to the formation of novel fullerene-containing supramolecular architectures with interesting optical and electronic properties.[20] Polypyridine units could be attached onto the nitrogen atoms of fulleropyrrolidines by the current bisaddition method and they are potential candidates for molecular electronics, since previous studies in our lab have shown the existence of direct electronic coupling between the pyridine nitrogen atom and the C_{60} core in fulleropyrrolidines.[21] Metal−ligand coordination has been studied as the key motif in the rational design of supramolecular linear arrays and large metallocyclic polygons.[22] Coordination driven self-assembly of these fullerene polypyridyl building blocks may lead to novel supramolecular architectures. For example, coordination of trans-1 C_{60} bisadducts to transition metal could generate a linear oligomeric structure and coordination of C_{60} equatorial bisadducts to transition metals may lead to the formation of square-shaped metallocycles (Figure 4). Our approach provides a general method for the selective synthesis of fulleropyrrolidine bisadducts such as trans-1, equatorial, and trans-3 adducts.

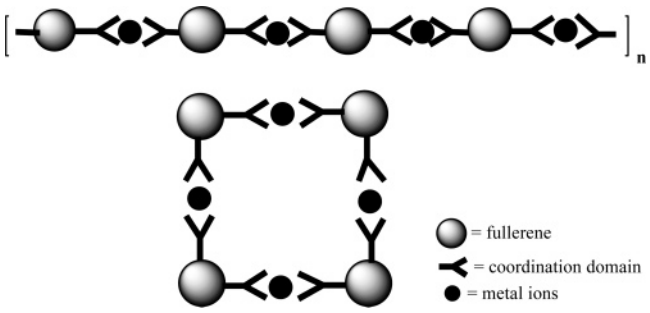


FIGURE 4. Conceptual description of coordination-driven self-assembly of fullerene-containing supramolecular structures. Top: Linear structure from trans-1 bisadducts. Bottom: Square-shaped structure from equatorial bisadducts.

The cleavage of the tether (phenyl or biphenyl) at the phenyl benzylic ether bond has been achieved by dealkylation with BBr_3, which led to the formation of two phenols attached on the α-carbon of the pyrrolidine rings in the resulting nontethered fulleropyrrolidine bisadducts.[23] A variety of functional groups can be incorporated into the bisadducts by reacting with the phenols.

Summary

In summary, we have established a general tether-directed approach for selective preparation of fulleropyrrolidine bisad-

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ducts with trans-1, trans-2, trans-3, trans-4, and equatorial bisaddition patterns, representing the first systematic study of this reaction, to the best of our knowledge. The nature of the tether linkages between the pyrrolidine rings is complicated by the unavoidable introduction of two new stereogenic centers. However, with the aid of computational studies, assignment of the structures of the bisadducts could be made from the spectral data. Most importantly, this approach provides a general access to the selective synthesis of fulleropyrrolidine bisadducts, where the same or different α-amino acids could be used. All of the bisadduct isomers could be purified by using flash column chromatography.

Experimental Section

General Procedure for the Synthesis of Bisaldehydes 1−4. To a solution of dibromide (10 mmol) and *p*-hydroxybenzaldehyde (2.95 g, 24 mmol) in 30 mL of DMF (dried with standard procedure) was added K_2CO_3 (4.14 g, 30 mmol). The mixture was stirred at 100 °C for 6−8 h until the complete consumption of dibromide monitored by TLC. Then the reaction mixture was cooled to room temperature and diluted with 30 mL of water, and the precipitates were collected through gravity filtration. TLC (CH_2Cl_2/EA, 95/5) showed it was pure product in most cases. If needed, column chromatography (silica, CH_2Cl_2/EA, 95/5) was used to further purify the products. The typical yield of this alkylation reaction was 75−82%. ^{1}H NMR (400 MHz $CDCl_3$) of **1**: δ 5.15 (s, 4H), 7.04 (d, 4H), 7.45 (s, 4H), 7.86 (d, 4H), 9.91 (s, 2H). ^{13}C NMR (100 MHz $CDCl_3$) of **1**: δ 69.9, 115.2, 128.0, 130.5, 132.1, 136.4, 163.7, 190.8. MALDI-MS: *m*/*z* 347.2 (MH^+). ^{1}H NMR (400 MHz $CDCl_3$) of **2**: δ 5.25 (s, 4H), 7.08 (d, 4H), 7.42 (dd, 2H), 7.53 (dd, 2H), 7.82 (d, 4H), 9.88 (s, 2H). ^{13}C NMR (100 MHz $CDCl_3$) of **2**: δ 68.5, 117.0, 129.1, 129.4, 130.4, 132.2, 134.3, 163.0, 191.0. MALDI-MS: *m*/*z* 347.4 (MH^+). ^{1}H NMR (400 MHz $CDCl_3$) of **3**: δ 5.18 (s, 4H), 7.08 (d, 4H), 7.42−7.47 (m, 3H), 7.52 (s, 1H), 7.86 (d, 4H), 9.90 (s, 2H). ^{13}C NMR (100 MHz $CDCl_3$) of **3**: δ 70.0, 115.2, 126.6, 127.5, 129.3, 130.2, 132.1, 136.9, 162.8, 191.5. MALDI-MS: *m*/*z* 347.2 (MH^+). ^{1}H NMR (400 MHz $CDCl_3$) of **4**: δ 5.25 (s, 4H), 7.11 (d, 4H), 7.52 (d, 4H), 7.65 (d, 4H), 7.85, (d, 4H), 9.93 (s, 2H). ^{13}C NMR (100 MHz $CDCl_3$) of **4**: δ 70.5, 115.2, 127.3, 128.0, 130.5, 132.1, 135.0, 140.5, 163.6, 190.7. MALDI-MS: *m*/*z* 422.8 (M^+).

General Procedure for the Synthesis of Fulleropyrrolidine Bisadducts. A mixture of C_{60} (36 mg, 0.05 mmol), sarcosine (7.2 mg, 0.40 mmol), and bisaldehydes **1**−**4** (0.05 mmol) in 10 mL of ODCB was refluxed for 4 h. The mixture was washed with H_2O twice, dried over Na_2SO_4, and concentrated. The residue was subjected to column chromatography with toluene/hexanes (70:30−90:10) as eluant. A typical flash column was a 30 mm × 300 mm silica column). Overall yields for bisadducts were in the range of 65−70%. ^{1}H NMR (400 MHz, acetone-d_6/CS_2 1:2) of bisadduct **5**: δ 2.55 (s, 3H), 2.62 (s, 3H), 3.94 (d, 1H), 4.20 (d, 1H), 4.32 (s, 1H), 4.59 (s, 1H), 4.87 (d, 1H), 4.93 (d, 1H), 4.96 (d, 1H), 5.03 (d, 1H), 5.11 (d, 1H), 5.24 (d, 1H), 6.74 (m, 4H), 7.15 (m, 1H), 7.30 (m, 1H), 7.38−7.44 (m, 6H). ^{13}C NMR (100 MHz acetone-d_6/CS_2 1:2) of bisadduct **5**: δ 40.1, 40.3, 68.4, 68.7, 68.9, 69.7, 70.4, 70.6, 76.5, 77.2, 83.0, 84.3, 128.4 (2C), 128.9, 129.3 (4C), 129.4, 129.7, 129.9 (4C), 135.3, 136.4, 137.2, 137.3 (2C), 137.6, 137.8 (2C), 139.7, 140.0, 141.2, 141.5, 141.8, 141.9 (2C), 142.0, 142.3, 143.0, 143.1, 143.4, 144.1, 144.4, 144.5, 144.7, 145.1, 145.2, 145.3, 145.5, 145.6, 145.7 (2C), 145.8, 145.9 (4C), 146.0, 147.6, 148.3, 148.5, 148.6, 148.8, 148.9, 149.0, 149.1, 149.4, 149.5, 149.7, 149.9, 150.1, 150.5, 153.8, 154.5, 155.4, 155.6, 157.2, 157.7, 158.3 (3C), 158.4, 158.8 (2C). MALDI-MS: *m*/*z* 1121.4 (MH^+). (See NMR and mass data of bisadducts **6**−**15** in the Supporting Information.)

General Procedure for the Synthesis of Fulleropyrrolidine Monoadducts. A mixture of C_{60} (36 mg, 0.05 mmol), sarcosine (3.6 mg, 0.20 mmol), and bisaldehydes **1**, **2**, **3**, or **4** (0.05 mmol) in 40 mL of toluene was refluxed for 3 h. The mixture was washed with H_2O twice, dried over Na_2SO_4, and concentrated. The residue was subjected to column chromatography (silica) with toluene as eluant. The typical yield for monoadduct was 70%. ^{1}H NMR (400 MHz $CDCl_3$) of **16**: δ 2.75 (s, 3H), 4.26 (d, 1H), 4.90 (s, 1H), 4.99 (d, 1H), 5.09 (s, 2H), 5.16 (s, 2H), 6.95 (d, 2H), 7.04 (d, 2H), 7.09 (m, 1H), 7.40 (m, 4H), 7.69 (m, 1H), 7.75 (d, 2H), 9.80 (s, 1H). ^{13}C NMR (100 MHz $CDCl_3$) of **16**: δ 40.5, 69.2, 69.8, 70.5 (2C), 78.2, 83.6, 115.5 (2C), 125.6, 128.5 (2C), 129.0, 129.5, 129.6, 131.0, 131.8 (2C), 136.5, 136.6, 136.7, 137.3, 137.5, 137.8, 140.2, 140.6, 140.8, 140.9, 142.2, 142.3, 142.5, 142.6, 142.7 (2C), 142.8, 142.9 (2C), 143.0 (2C), 143.1 (2C), 143.2, 143.3, 143.4, 143.7, 143.9, 145.1 (2C), 145.4, 145.5, 145.8, 145.9 (2C), 146.0 (2C), 146.1, 146.2, 146.3 (2C), 146.4, 146.5, 146.6 (2C), 146.8, 146.9 (2C), 147.0 (2C), 147.2, 147.4, 147.6, 147.9, 154.5, 154.9, 157.3, 159.5, 164.2, 189.9. MALDI-MS: *m*/*z* 1066.2 (M^+). (See NMR and mass data of monoadducts **17**−**19** in the Supporting Information.)

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Supporting Information Available: NMR and mass data of bisadducts **6**−**15** and monoadducts **17**−**19** and selected spectra and AM1 calculation findings. This material is available free of charge via the Internet at http://pubs.acs.org.

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