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Approaches to Open Fullerenes: Synthesis and Thermal Stability of *cis-1* Bis(isobenzofuran) Diels−Alder Adducts of C_{60}

Michael Sander, Thibaut Jarrosson, Shih-Ching Chuang, Saeed I. Khan, and Yves Rubin*

Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095-1569

rubin@chem.ucla.edu

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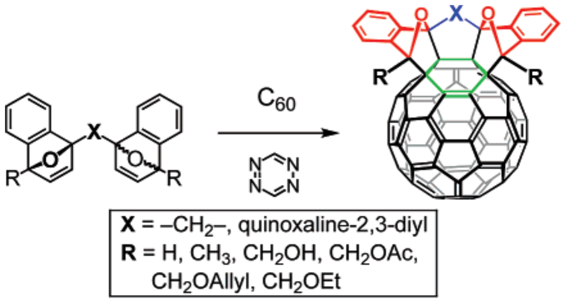

In a quest to form wider openings within the cage of the fullerene C_{60} through controlled bond-breaking reactions, we have examined the double saturation of adjacent $C=C$ bonds within a six-membered ring of C_{60}. We have investigated the double Diels−Alder cycloaddition of two tethered isobenzofurans to the fullerene C_{60}. We obtained *cis-1* adducts in good yields after reacting the methylene- or quinoxaline-tethered bis(isobenzofuran) precursors **2a**−**k** with parent 3,6-dihydro-1,2,4,5-tetrazine (**3b**). The X-ray structure of the methylene-tethered bis(isobenzofuran)-C_{60} adduct **4b** has been obtained; four-eclipsed substituents are held rigidly by the bicyclic addends. The *cis-1* bis(isobenzofuran) bisadducts **4b** and **4e**−**j** are kinetically far more stable toward thermal retro-Diels−Alder fragmentation than are mono-(isobenzofuran) adducts of C_{60}, in solution and in the solid state as determined by ^{1}H NMR spectroscopy or thermogravimetric analysis. A methodology for the reversible solubilization of other fullerene derivatives based on this work is also presented.

Introduction

In the preceding paper, we reported on the cycloaddition of mono- and disubstituted isobenzofurans to the fullerene C_{60} to form Diels−Alder monoadducts.[1] In the present work, we have studied the tandem addition of two tethered isobenzofuran units to adjacent double bonds of C_{60} (*cis-1* addition pattern), in a stepwise approach to saturating all three double bonds of a six-membered ring.[2] Contrary to the isobenzofuran monoadducts, all bisadducts **4b** and **4e**−**j** were found to be highly kinetically stable toward retro-Diels−Alder fragmentation. They are ideal precursors of the desired 1,2,3,4,5,6-hexaadducts that would be formed by generation of reactive species from two side chains of the oxabicyclic units, to facilitate the final $C=C$ bond saturation; this approach follows "Strategy 2" presented in the preceding paper.[1,3]

Herein, we report the syntheses of *cis-1* bis(isobenzofuran)-C_{60} adducts **4b** and **4e**−**j** and discuss the effects of the different linkages separating the two isobenzofuran units on the reaction outcome. A number of tethered addend systems have been used for the functionalization of C_{60} in a variety of addition patterns,[4] which were especially useful for highly disfavored patterns such

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(1) See the preceding article in this issue: Chuang, S.-C.; Jarrosson, T.; Sander, M.; James, S.; Rozumov, E.; Khan, S. I.; Rubin, Y. *J. Org. Chem.* **2007**, *72*, 2716−2723.

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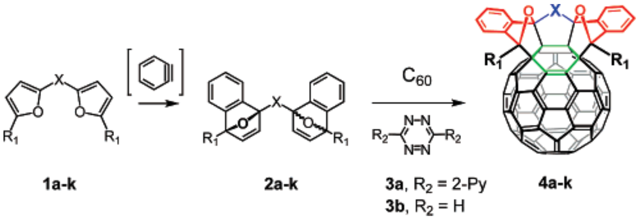
(3) Chuang, S.-C.; Clemente, F. R.; Khan, S. I.; Houk, K. N.; Rubin, Y. *Org. Lett.* **2006**, *8*, 4525−4528.

(4) (a) Diederich, F.; Gómez-López, M. *Chem. Soc. Rev.* **1999**, *28*, 263−277. (b) Diederich, F.; Kessinger, R. *Acc. Chem. Res.* **1999**, *32*, 537−545. (c) Qian, W.; Rubin, Y. *Angew. Chem., Int. Ed.* **2000**, *39*, 3133−3137. (d) Qian, W.; Rubin, Y. *J. Am. Chem. Soc.* **2000**, *122*, 9564−9565. (e) Qian, W.; Rubin, Y. *Angew. Chem., Int. Ed.* **1999**, *38*, 2356−2360. Herzog, A.; Hirsch, A.; Vostrowsky, O. *Eur. J. Org. Chem.* **2000**, 171−180. (f) Djojo, F.; Hirsch, A.; Grimme, S. *Eur. J. Org. Chem.* **1999**, 3027−3039. (g) Echegoyen, L. E.; Djojo, F. D.; Hirsch, A.; Echegoyen, L. *J. Org. Chem.* **2000**, *65*, 4994−5000. (h) Reuther, U.; Brandmüller, T.; Donaubauer, W.; Hampel, F.; Hirsch, A. *Chem. Eur. J.* **2002**, *8*, 2261−2273. (l) Thilgen, C.; Diederich, F. *C. R. Acad. Sci., Ser. IIc: Chim.* **2006**, *9*, 868−880.

10.1021/jo061987b CCC: \$37.00

TABLE 1. General Route for the Double Diels−Alder Cycloadditions of Bis(isobenzofuran)s 2a−2k to Fullerene C_{60}

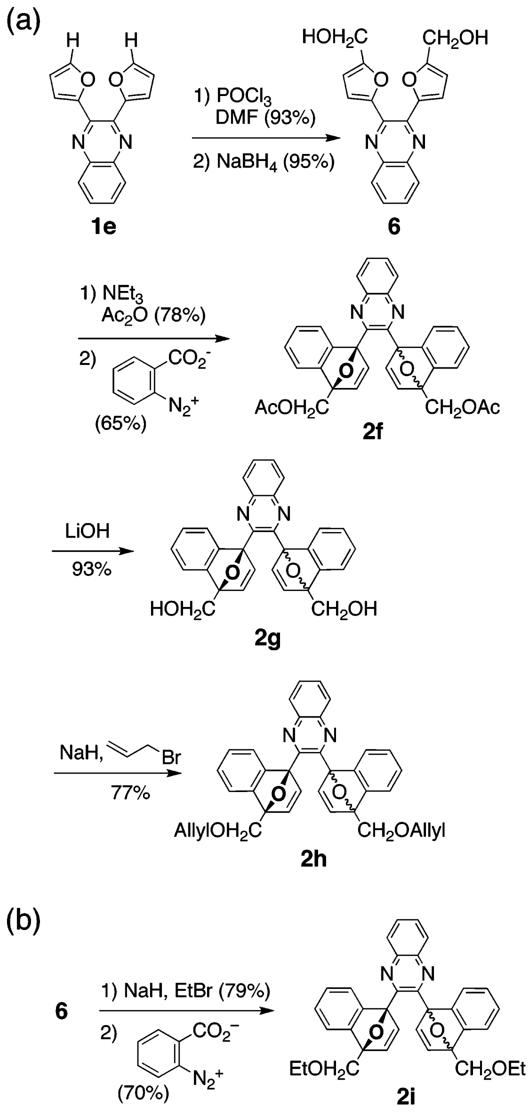


precursor	X	R_1	**4a−k** yield (%)[a] (**3a**, 45 °C)	(**3b**, 25 °C)
2a	S	CH_2OAc		
2b	CH_2	H	50[b] (57)	
2c	CH_2	CO_2Me		
2d	$C(CH_3)_2$	H		
2e	quinoxaline-2,3-diyl	H		36 (47)
2f	quinoxaline-2,3-diyl	CH_2OAc		8.6 (32)
2g	quinoxaline-2,3-diyl	CH_2OH		49 (77)
2h	quinoxaline-2,3-diyl	$CH_2OCH_2CH{=}CH_2$		4 (25)
2i	quinoxaline-2,3-diyl	CH_2OEt		13 (33)
2j	quinoxaline-2,3-diyl	CH_3		56 (92)
2k	CH_2OCH_2	CH_2OAc	c	

[a] Yields in parenthesis are based on recovered C_{60}. [b] Besides *cis-1* adduct **4b**, mono(isobenzofuran) adduct **4b′** was also isolated in 2.8% (3.2%) yield with its second isobenzofuran precursor unit intact. [c] Mono(isobenzofuran) adduct **4k′** was isolated in 73% yield (81%).

as the *trans-1* ("polar caps") position of C_{60}.[5] Although it is energetically and electronically possible to functionalize the *cis-1* position despite more stringent steric bias in the second addition,[6] there are only a few examples of this pattern that are known.[7] We wanted a general approach to *cis-1* bisadducts and chose to test tandem Diels−Alder cycloadditions using two reactive isobenzofuran units tethered by various linkers such as sulfide, methylene, $C(CH_3)_2$, 2,3-quinoxaline-diyl, and the CH_2OCH_2 unit. Of these linkages, we found that the one-carbon methylene (**4b**) and two-carbon 2,3-quinoxaline linkers (**4e−j**) were the most suitable systems because they position the second approaching isobenzofuran unit in close proximity to the *cis-1* C═C bond, and most importantly, they favor a suitable geometry of approach in the transition state. The S, $C(CH_3)_2$, and CH_2OCH_2 linkers, however, did not result in the corresponding *cis-1* bisadducts (**4a**, **4c**, **4d**, **4k**), from either unfavorable electronics (**4a**), excessive steric hindrance (**4c**, **4d**), or poor angle of approach for the second addition (**4k**). These results were correlated by theoretical calculations that show that the number of linking atoms (1−3) between the two isobenzofuran units has a strong influence on the transition state energies due to more or less favorable angles of approach.

SCHEME 1



Results and Discussion

Synthesis of Bis(isobenzofuran) Precursors 2a−k. The bis(isobenzofuran) precursors **2a−k** were prepared using five different linkers, namely, S, CH_2, CMe_2, quinoxaline-2,3-diyl, and CH_2OCH_2 units (Table 1, Schemes 1−3), through in situ double [4 + 2] cycloaddition of benzyne to bisfurans **1a−k**, based on the method described in our accompanying paper.[1,8] As expected, these reactions resulted in mixtures of syn and anti diastereomers, which we isolated chromatographically. The syntheses of the bis(isobenzofuran) precursors **2a−e** were performed using known procedures.[9] The syntheses of precursors **2f−i** (Scheme 1) began with the 2,3-bisfurylquinoxaline **2e** undergoing Vilsmeier−Haack formylation and subsequent

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(5) (a) Bourgeois, J.-P.; Echegoyen, L.; Fibbioli, M.; Pretsch, E.; Diederich, F. *Angew. Chem., Int. Ed.* **1998**, *37*, 2118−2121. (b) Qian, W.; Rubin, Y. *J. Am. Chem. Soc.* **2000**, *122*, 9564−9565. (c) Qian, W.; Rubin, Y. *Angew. Chem., Int. Ed.* **1999**, *38*, 2356−2360. (d) Qian, W.; Rubin, Y. *Angew. Chem., Int. Ed.* **2000**, *39*, 3133−3137. (e) Qian, W.; Rubin, Y. *J. Org. Chem.* **2002**, *67*, 7683−7687.

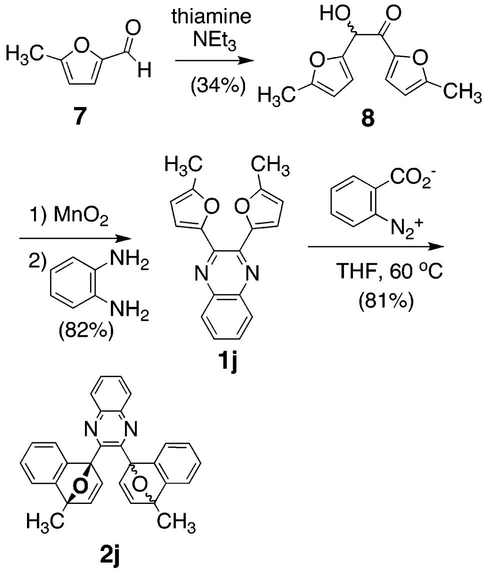
(6) (a) Hirsch, A.; Lamparth, I.; Karfunkel, H. R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 437−438. (b) Reuther, U.; Brandmüller, T.; Donaubauer, W.; Hampel, F.; Hirsch, A. *Chem. Eur. J.* **2002**, *8*, 2261−2273.

(7) (a) Jensen, A. W.; Khong, A.; Saunders, M.; Wilson, S. R.; Schuster, D. I. *J. Am. Chem. Soc.* **1997**, *119*, 7303−7307. (b) Kanakamma, P. P.; Huang, S. L.; Juo, C. G.; Her, G. R.; Luh, T. Y. *Chem. Eur. J.* **1998**, *4*, 2037−2042. (c) Hsiao, T. Y.; Chidambareswaran, S. K.; Cheng, C. H. *J. Org. Chem.* **1998**, *63*, 6119−6122. (d) Rubin, Y.; Ganapathi, P. S.; Franz, A.; An, Y.-Z.; Qian, W.; Neier, R. *Chem. Eur. J.* **1999**, *5*, 3162−3184.

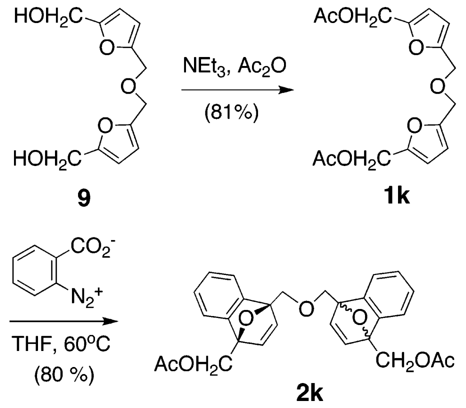
(8) Stiles, M.; Miller, R. G. *J. Am. Chem. Soc.* **1960**, *82*, 3802.

(9) See Experimental Section.

SCHEME 2



SCHEME 3

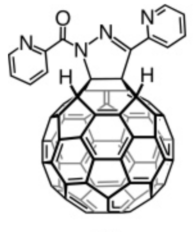


reduction to the diol **6**. This diol was converted to its bis(ethyl ether) **1i** and then reacted with benzyne to produce the bis(isobenzofuran) precursor **2i**. The diol **6** was also converted to the diester bis(isobenzofuran) precursor **2f** by first protecting the hydroxyl groups using acetic anhydride and then performing the benzyne additions. Removal of the ester units of **2f** with lithium hydroxide produced the diol **2g**, which was converted into the bis(allyl ether) **2h**.

The dimethyl bis(isobenzofuran) precursor **2j** was prepared (Scheme 2) through the acyloin condensation of aldehyde **7** to form α-furoin **8**, oxidation (manganese dioxide) and immediate condensation (*o*-phenylenediamine) of **8** to produce the bisfurylquinoxaline **1j**, and subsequent benzyne addition. The CH_2OCH_2-tethered bis(isobenzofuran) precursor **2k** was readily synthesized (Scheme 3) by acetylating bisfuran-diol **9** to produce **1k** and then subjecting this diester to benzyne addition.

Additions of Bisisobenzofurans to C_{60}. We applied a modification of Warrener's methodology to generate the reactive isobenzofurans in one-pot processes, using the approach we described in the previous paper.[1] The conventionally used 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (**3a**) did not always generate the isobenzofuran effectively because of the very high steric demand of the bisisobenzofuran precursors **2a**−**k**. We used the much more reactive parent 3,6-dihydro-1,2,4,5-tetrazine (**3b**) as the inverse-electron-demand Diels−Alder reactant.

3,6-Dihydro-1,2,4,5-tetrazine (**3b**) was prepared following the method described by Sauer et al.[10] Unfortunately, this synthesis usually provides the tetrazine in an overall yield below 10% and as a CH_2Cl_2 solution. We found that it was preferable to perform the syntheses of the *cis-1* adducts in *o*-dichlorobenzene rather than toluene for optimal solubilization. The syntheses of the *cis-1* adducts were optimized by adjusting both the amount of added 3,6-dihydro-1,2,4,5-tetrazine (**3b)** and the total reaction time. Generally, we added 4 equiv of tetrazine to solutions of the bis(isobenzofuran) precursors **2b** and **2e**−**k**, along with C_{60} and then performed the reactions for no longer than 2.5 h to avoid the isolation of the byproducts **10** or **11**, which arise from the direct addition of the tetrazines **3a** or **3b** with C_{60}.[11] Table 1 lists the various *cis-1* C_{60} bisadducts synthesized generally in moderate yields (30−60%). The characterization of all isolated *cis-1* adducts is based on their ^1H, ^{13}C, and MS spectral data. For examples, compound **4e** displays a unique sp^3 proton signal at 6.73 ppm in the ^1H NMR spectrum. Two distinct oxa-bridged sp^3 carbons at 88.51 and 94.71 ppm and another two sp^3 carbons on the C_{60} framework at 72.79 and 77.48 ppm are observed in ^{13}C NMR spectrum, reflecting the C_s-symmetry of this compound.



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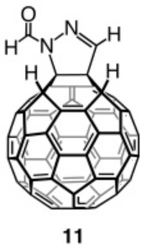

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Effects of the Linkers. Among the bis(isobenzofuran)s containing a one-atom linker, we chose the sulfur-linked bis(isobenzofuran) precursor **2a** for our initial tests of Warrener's methodology for generating isobenzofurans. Thus, we treated **2a** with 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (**3a**) and C_{60} at 45 °C, using the same procedure we had used for the preparation of the mono(isobenzofuran)-C_{60} adducts.[1] Unfortunately, we did not observe (TLC) any new C_{60} derivative. Another trial reaction, using the more reactive 3,6-dihydro-1,2,4,5-tetrazine (**3b**) at room temperature, also failed to produce the desired product. It is likely that the sulfur linker is too stabilizing on the isobenzofuran units, making them less reactive toward [4 + 2] cycloaddition with C_{60} as a result of conjugation between the lone pairs of sulfur and the π systems of the furans.

To avoid this issue, we investigated the reactivity of the methylene-bridged bis(isobenzofuran) precursor **2b**. Under similar conditions, when using 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (**3a**), we observed that two C_{60} derivatives (**4b** and **4b′**, Table 1 and structure below) formed in the reaction mixture. The first of the products to elute by chromatography on silica gel was the monoadduct **4b′** having its other isobenzofuran precursor unit intact, revealing the low propensity for a second

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[10] (a) Sauer, J. In *Comprehensive Heterocyclic Chemistry 2*; Pergamon Press: Oxford, 1996; Vol. 6, pp 901−957. (b) Sauer, J.; Heldmann, D. K.; Hetzenegger, J.; Krauthan, J.; Sichert, H.; Schuster, J. *Eur. J. Org. Chem.* **1998**, 2885−2896.

[11] (a) Murata, Y.; Suzuki, M.; Rubin, Y.; Komatsu, K. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 1669−1672. (b) Miller, G. P.; Tetreau, M. C.; Olmstead, M. M.; Lord, P. A.; Balch, A. L. *Chem. Commun.* **2001**, 1758−1759.

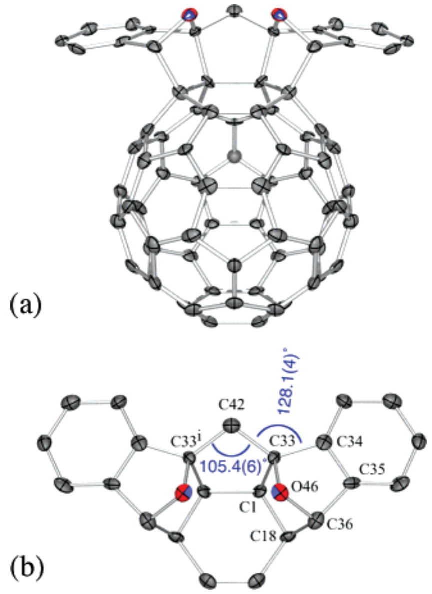
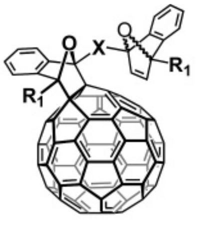


FIGURE 1. Crystal structure of the *cis-1* bisadduct **4b**. (a) Ortep drawing with 30% probability. (b) Top view of the structure with all sp^2 carbons of the C_{60} moiety omitted for clarity.

addition of tetrazine **3a** on this sterically hindered intermediate. The second compound to elute was characterized as the desired bis(isobenzofuran) adduct **4b**, most conclusively through its X-ray crystallographically determined single-crystal structure (Figure 1a), which indicated that it is the expected *cis-1* bisadduct. In contrast, we did not observe the formation of any isobenzofuran adducts from precursor **2c**, which is the related methylene-bridged system possessing CO_2Me functional groups. This lack of reactivity may be explained by our previous observation that an ester-substituted mono adduct was very labile at a reaction temperature of 45 °C.[1] The *gem*-dimethylmethylene-bridged precursor **2d** also failed to yield any C_{60} adducts, presumably because of the steric hindrance imparted by the endo-oriented methyl group during the approach of the second isobenzofuran unit at the C_{60} surface.



4b′, X = CH_2, R_1 = CO_2Me
4k′, X = CH_2OCH_2, R_1 = CH_2OAc

The crystal structure of *cis-1* adduct **4b** has several features indicative of the large amount of strain that is created in the two-step additions of isobenzofuran units to C_{60}. With only a one-atom link between the isobenzofuran units, high torsional strain is created during the second Diels−Alder reaction. This is shown by the strong extension of bond angle for the C34−C33−C42 connecting carbons, at 128.1(4)°, well away from the ideal sp^3 angle (109.5°). The C33−C42−C33^i bond angle of the methylene connecting unit is 105.4 (6)°, about 4° less than the normal sp^3 hybridized carbon angle. The angles and bond lengths for the oxa-bridged moieties are similar to those of the mono(isobenzofuran)-C_{60} structure discussed in the accompanying paper.[1] The lengths of the bonds connecting the addend with the fullerene framework are significantly different at 1.605(7) Å for the C1−C33 bond and 1.573(7) Å for the C18−C36 bond, respectively. This may reflect steric compression and the high strain in the methylene bridge linking the two added units.

Having successfully isolated the bis(isobenzofuran) *cis-1* bisadduct **4b** possessing the one-atom (CH_2) linker, we became interested in the possibility of forming bis(isobenzofuran) *cis-1* bisadducts featuring longer linkers. After considering many of the options available for a two-atom tether, we chose to use the quinoxaline-2,3-diyl linker because 2,3-bisfurylquinoxaline can be readily prepared from commercially available furfural in a few steps and on a large scale.[12] In principle, 2,3-bisfurylquinoxaline can be used as a building block for preparing a number of other bis(isobenzofuran) precursors because the C5 position of the furyl group is readily functionalized, e.g., through Vilsmeier−Haack formylation.[13] When we treated the bis(isobenzofuran) precursor **2e** with tetrazine **3b** and C_{60}, we isolated the *cis-1* bis(isobenzofuran) bisadduct **4e** as the only addition product. Hence, in this case all of the intermediate monoadduct was consumed, significantly reducing the difficulty of isolating the desired product. Next, we examined the reactions of the corresponding bis(isobenzofuran) precursors possessing CH_3, CH_2OH, CH_2OAc, CH_2OEt, and $CH_2OAllyl$ functionalities at the C5 positions of the furan units. These precursors, **2f**−**j**, all readily generated reactive bis(isobenzofuran)s upon treatment with 3,6-dihydro-1,2,4,5-tetrazine (**3b**) and subsequently provided the *cis-1* bisaddition derivatives **4f**−**j** in moderate-to-good yields.

Finally, we examined the feasibility of extending the length of the linker connecting the isobenzofuran units to three atoms. Reaction of the bis(isobenzofuran) **2k** containing a CH_2OCH_2 tether did not lead to the formation of any *cis-1* bisadduct; only the mono-addition product **4k′** was isolated. This result shows that, with this linker, the second isobenzofuran unit cannot be positioned efficiently in its approach of the *cis-1* C=C double bond, as shown in the calculations reported below.

Computational Considerations. To understand more thoroughly the effects that the different linkers have on the formation of *cis-1* bisaddition products, we used the AM1, PM3, B3LYP/3-21G*//PM3, and B3LYP/6-31G*//PM3 levels of theory to compute the relative energies for each addition of the CH_2-, quinoxaline-2,3-diyl-, and CH_2OCH_2-linked bis(isobenzofuran)s to C_{60}; Table 2 summarizes the results. The values we obtained using the B3LYP/6-31G*//PM3 method coincided best with the experimental results. Generally, the addition of the first isobenzofuran unit was energetically favored for all three of these linkers: it was exothermic for the CH_2- and CH_2OCH_2-linked systems (by -7.4 and -6.3 kcal mol^{-1}, respectively) and slightly endothermic for the quinoxaline-2,3-diyl linker (by $+4.3$ kcal mol^{-1}). The addition of the second isobenzofuran moiety was much more energetically favored for the 2,3-quinoxaline-linked system (exothermic by -17.5 kcal mol^{-1}) than were those of the CH_2- and CH_2OCH_2-linked systems. The calculated endothermicity of the second addition of the CH_2-

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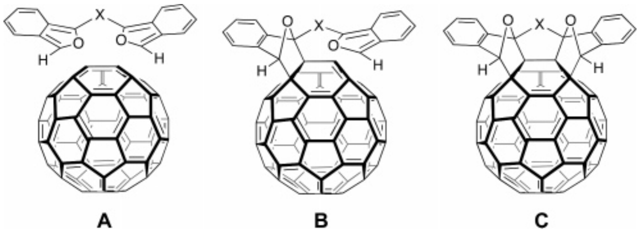
[12] (a) Stetter, H.; Ramsch, R. Y.; Kuhlmann, H. *Synthesis* **1976**, 733−736. (b) Firouzabadi, H.; Karimi, B.; Abbassi, M. *Chem. Res., Synop*. **1999**, *3*, 236−237. (c) Abdel-Jalil, J.; Al-Qawasmeh, R. A.; Voelter, W.; Heeg, P.; El-Abadelah, M. M.; Sabri, S. S. *J. Heterocycl. Chem.* **2000**, *37*, 1273−1275.

[13] Vilsmeier, A.; Haack, A. *Ber*. **1927**, *60*, 119.

TABLE 2. Relative Heats of Formation between C_{60} and a Theoretical Intermediate Bisisobenzofuran (A), an Intermediate Monoadduct (B), and Bisadduct (C) in the Stepwise Addition of Linked Bis(isobenzofuran)s to C_{60}

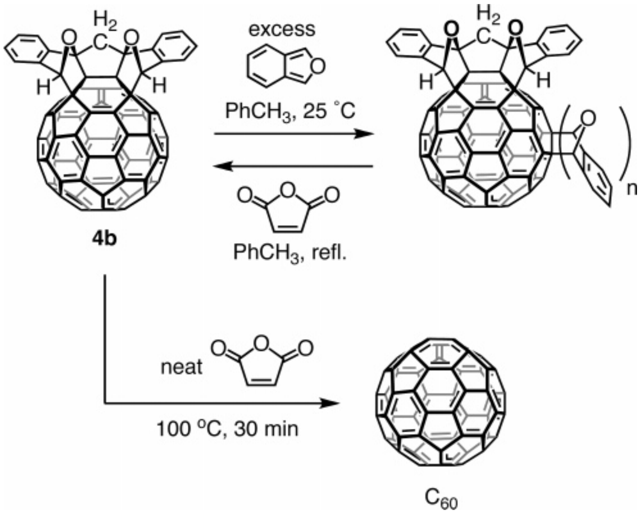


linker X	method	relative energy (kcal mol^{-1}) A	B	C
CH_2	AM1	0	−26.1 (0)	−42.7 (−16.6)
	PM3	0	−25.9 (0)	−46.8 (−20.8)
	B3LYP/3-21G*//PM3	0	−23.8 (0)	−46.1 (−22.3)
	B3LYP/6-31G*//PM3	0	−7.4 (0)	−10.6 (−3.2)
quinoxaline-2,3-diyl	AM1	0	−22.4 (0)	−42.5 (−20.1)
	PM3	0	−21.8 (0)	−43.0 (−21.1)
	B3LYP/3-21G*//PM3	0	−14.9 (0)	−39.4 (−24.5)
	B3LYP/6-31G*//PM3	0	+4.3 (0)	−13.2 (−17.5)
CH_2OCH_2	AM1	0	−28.2 (0)	−29.3 (−1.0)
	PM3	0	−27.3 (0)	−32.8 (−5.5)
	B3LYP/3-21G*//PM3	0	−24.6 (0)	−28.4 (−3.8)
	B3LYP/6-31G*//PM3	0	−6.3 (0)	−4.0 (+10.3)

OCH_2-linked system (+10.3 kcal mol^{-1}) reflects the fact that this reaction is hindered by unfavorable torsional constraints in the approach of the second isobenzofuran unit to the fullerene *cis-1* bond.

Thermal Stability of the *cis-1* Bis(isobenzofuran) C_{60} Adducts. The *cis-1* bisadducts **4b** and **4e**−**j** were remarkably more stable thermally than the mono(isobenzofuran)-C_{60} adducts,[1] both in solution and in the solid state. For example, in solutions of toluene (bp 110 °C) or diphenyl ether (bp 259 °C) under reflux, we observed no decomposition of **4b** in the presence of a trapping reagent (*N*-methylmaleimide). The only conditions under which we observed addend loss occurred when we treated the *cis-1* bisadduct **4b** with neat molten maleic anhydride at 100 °C. Scheme 4 provides a comparison of the drastic differences in stability that exist between the mono- and bisadducts. When we treated the *cis-1* bisadduct **4b** with a large excess of isobenzofuran, generated from the reaction of 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (**3a**) and 1,4-epoxynaphthalene,[14] we obtained a mixture of regioisomeric multiadducts of pale orange color. In refluxing toluene in the presence of maleic anhydride, the appended mono(isobenzofuran) moieties were readily removed from these multiadducts, whereas heating in neat maleic anhydride was necessary to remove the tethered bis(isobenzofuran) addend. In addition, the molecular ions of the various bis(isobenzofuran) adducts were readily obtained using FAB mass spectrometry, whereas those of the mono(isobenzofuran) adducts were barely detected, if at all, further showing the added stability imparted by the *cis-1* addend.

SCHEME 4



We used thermogravimetric analysis (TGA) to investigate the solid-state stability of these bis(isobenzofuran) adducts under argon. Figure 2 displays the percentage weight losses of **4b** and **4e** that occurred upon heating. Contrary to the TGA experiments that we performed for the monoisobenzofuran adducts in our accompanying paper,[1] the percentages of mass losses for the bisadducts **4b** and **4e** are complicated by their polymerization during heating (insoluble black powders were recovered after heating to 850 °C). For both samples, we observed two main steps in the losses of mass in addition to the initial loss of the solvent of crystallization (toluene) around 100−150 °C. For methylene-bridged adduct **4b**, the first step corresponds to the decomposition and evaporation of the isobenzofuran moiety for ca. 20% (26% theoretically), starting from 300 °C and spanning to ∼420 °C. The second step corresponds to the sublimation of C_{60} up to 820 °C (the polymeric material recovered accounted for total mass balance). In contrast, *cis-1* adduct **4e** began to decompose and evaporate much less cleanly starting at 300 °C. The estimated mass loss in the first step is 20%, much less than that of the theoretical value (33%) and likely accounted for by trapping of the bisisobenzofuran units through crosslinking of fullerene units in the solids.

UV−vis Spectra of *cis-1* Bis(isobenzofuran) C_{60} Adducts. Figure 3 shows that the UV−vis absorption spectra of the representative *cis-1* bis(isobenzofuran) adducts **4b**, **4e**, and **4j** exhibit a characteristic peak at 427 nm, which is similar to the characteristic absorption at 432 nm that is displayed by mono(isobenzofuran)-C_{60} adducts.[1] This absorption band is also relatively close to the typical absorption peak observed at ca. 426 nm for other C_{60} monoadducts.[15] These absorptions features also reflect those of the other known *cis-1* bisadducts.[16]

Conclusion

The double [4 + 2] cycloaddition of tethered bis(isobenzofuran) systems can be readily performed with C_{60}. These

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[14] (a) Warrener, R. N. *J. Am. Chem. Soc.* **1971**, *93*, 2346−2348. (b) Friedrichsen, W. *Adv. Heterocycl. Chem.* **1980**, *26*, 135−241. (c) Rodrigo, R. *Tetrahedron* **1988**, *44*, 2093−2135. (d) Rickborn, B. In *Advances in Theoretically Interesting Molecules*; Thummel, R. P., Ed.; JAI Press Inc.: Greenwich, CT, 1989; Vol. I, pp 1−134. (e) Bird, C. W. *Prog. Heterocycl. Chem.* **1990**, *2*, 87−101. (f) Peters, O.; Friedrichsen, W. *Trends Heterocycl. Chem.* **1995**, *4*, 217−259.

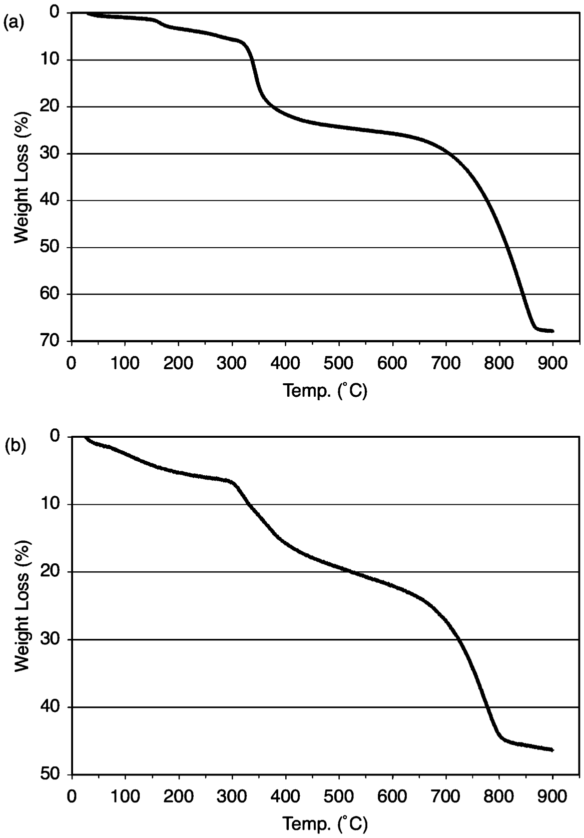

FIGURE 2. Thermogravimetric analyses of (a) compound **4b** and (b) compound **4e**.

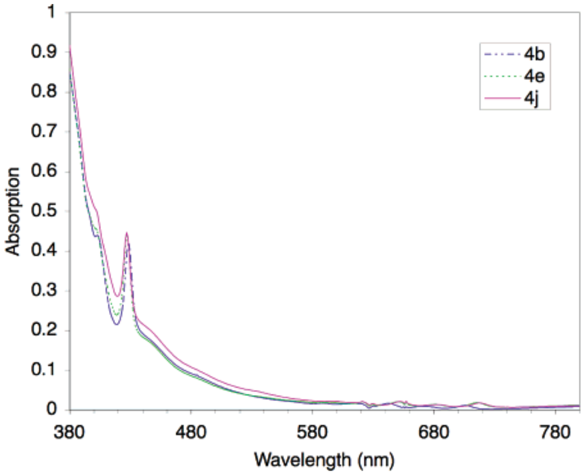

FIGURE 3. UV−vis absorption spectra of *cis-1* bisadducts **4b**, **4e**, and **4j**.

syntheses were performed by treating the bis(isobenzofuran) precursors **2b** and **2e**−**j** with tetrazines **3a** or **3b** and C_{60}. Successful synthesis of the *cis-1* bisadduct required an appropriate tether between the two isobenzofuran moieties to provide a favorable geometric configuration and distance between the two adding reactive groups. Using this approach, the saturation of two of the three C=C double bonds within a six-membered ring of C_{60} can be easily performed. This methodology provides the means of saturating the remaining double bond of a six-membered ring of C_{60} via the side chains of the isobenzofurans with suitably reactive functional groups.[3]

Experimental Section

X-ray Data for Compound 4b. A black crystal (approximate dimensions 0.20 × 0.10 × 0.10 mm) was used for X-ray crystallographic analysis. The X-ray intensity data were measured at 100(2) K on an X-ray diffractometer system equipped with a Mo-target X-ray tube ($\lambda = 0.71073$ Å) operated at a power of 2250 W. A total of 1321 frames were collected at a scan width of 0.3° in ω and an exposure time of 90 s frame^{-1}. The frames were integrated using the SAINT software package with a narrow-frame integration algorithm. Integration of the data using a monoclinic unit cell yielded a total of 35,674 reflections, to a maximum 2θ angle of 56.58°, of which 19,360 were independent and 9400 were greater than $4\sigma(F)$. The final cell constants [$a = 20.310(4)$ Å, $b = 20.105(3)$ Å, $c = 27.042(5)$ Å, $\beta = 99.637(3)°$, $V = 10{,}887(3)$ Å^3] are based upon the refinement of the XYZ centroids of 1024 reflections above $20\sigma(I)$. Analysis of the data showed that negligible decay occurred during data collection. The structure was refined using the SHELXTL (v 6.12) software package, with the space group *Cm*. The final anisotropic full-matrix least-squares refinement on F^2 converged at $R_1 = 0.056$, $wR_2 = 0.112$, and a goodness-of-fit of 0.883. The largest peak on the final difference map was 0.984 e Å^{-3}.

General Procedure A. Preparation of Isobenzofuran Precursors. The benzyne precursor was prepared using the following typical procedure. Generally, ∼3 equiv of anthranilic acid was used with respect to 1 equiv of bisfurans. For example, isoamyl nitrite (5.0 mL, 38 mmol) was added to a solution of anthranilic acid (2.45 g, 17.9 mmol) and trichloroacetic acid (34 mg, 0.21 mmol) in THF (30 mL) at 0 °C. The resulting solution was stirred vigorously for a few minutes at 0 °C and then warmed to room temperature. After stirring for 1 h at room temperature, the color of the solution had turned pale yellow. The solids (**Caution! Danger of explosive decomposition!** No metal spatula) were collected in a Buchner funnel (paper filter) and collected by washing with dry THF into a flask containing the bisfuran derivatives **2a**−**k** (6.0 mmol). Propylene oxide (2 mL) and dry THF were added until the total volume was ca. 60 mL. The resulting mixture was then gradually heated to 60 °C. The diazonium salt decomposed gradually to generate benzyne. After 1 h, the decomposition of the diazonium carboxylate salt was complete, and the solution was heated under reflux for several minutes. The solution was then concentrated to a volume of ca. 4 mL and purified by silica gel chromatography using appropriate eluents. See experimental description and spectral data for compounds **2b**−**e** and **2i**−**k** in the Supporting Information.

Synthesis of S-Bridged Benzyne Adduct 2a. The S-bridged bisfuran **1a** was synthesized according to the known procedure.[17] Double Diels−Alder reaction with benzyne gave the adduct **2a** according to general procedure A using 3.43 g (25 mmol) of anthranilic acid, 6.3 mL (48 mmol) of isoamyl nitrite, and 2.17 g (7.0 mmol) of the bisfuran **1a**. Yield: 1.58 g (49%). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 2.14 (s, 6H), 4.80 (d, $J = 12.6$ Hz, 2H), 5.00 (d, $J = 12.6$ Hz, 2H), 6.74 (d, $J = 5.3$ Hz, 2H), 7.00−7.02 (m, 6H), 7.12−7.14 (m, 2H), 7.57−7.59 (m, 2H). ^{13}C NMR

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(17) (a) Chute, W. J.; Orchard, W. M.; Wright, G. F. *J. Org. Chem.* **1941**, *6*, 157−168. (b) Nazarova, Z. N.; Potemkin, G. F. *Zh. Obshchei Khim.* **1965**, *1*, 1709−1710.

(125.7 Hz, $CDCl_3$) δ (ppm) 20.7, 61.0, 90.2, 96.5, 118.8, 122.2, 125.2, 125.5, 141.0, 142.0, 146.2, 147.6, 149.2, 170.7. FT-IR (KBr) ν (cm^{-1}) 3065, 2941, 1741, 1366, 1227, 1171, 1103, 1037, 960, 759, 734. HRMS-EI (*m/z*) calcd for $C_{26}H_{22}O_6S$ 462.1137, found 462.1149.

2,3-Bis(5-formyl-2-furyl)quinoxaline (5). Freshly distilled $POCl_3$ (47 mL) was cautiously added to a solution of dry DMF (43 mL, 550 mmol) in dry 1,2-dichloroethane (100 mL) at 0 °C. The resulting mixture was stirred for 30 min at 20 °C, and then the bisfuran **5** (26.2 g, 0.1 mol) was added as a solid in one portion. Stirring was continued at 20 °C for 2 h; to complete the reaction, the mixture was finally heated under reflux for 1 h. During this time, the starting material slowly dissolved, and upon heating the color of the solution darkened and then a clear solution was obtained. After cooling to 20 °C, the reaction mixture was poured into a solution of sodium acetate trihydrate (340 g, 2.5 mol) in water (1.5 L) without further cooling. This mixture was stirred for ca. 30 min while small portions of solid $NaHCO_3$ (total 200 g) were added. CH_2Cl_2 (1 L) was added to dissolve the precipitated dialdehyde, and then the biphasic system was filtered through a plug of celite to remove a small amount of resinous material. After rinsing the plug with some CH_2Cl_2, the combined layers were separated, and the aqueous phase was extracted with CH_2Cl_2. The combined organic extracts were washed with a saturated $NaHCO_3$ solution until the pH was neutral and then dried (sodium sulfate). Activated charcoal (15 g) and silica gel (30 g) were added to the drying mixture, which was then passed through a plug of celite. Evaporation of the solvent provided a yellow solid, which was treated with methanol (50 mL), collected on a Büchner funnel, and finally air-dried to give dialdehyde **7** (29.7 g, 93%) as a crystalline material, mp 217 °C. ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.20 (d, *J* = 3.7 Hz, 2H), 7.41 (d, *J* = 3.7 Hz, 2H), 7.87 (dd, *J* = 6.4, 3.4 Hz, 2H), 8.18 (dd, *J* = 6.4, 3.4 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 114.7, 121.5, 129.4, 131.8, 141.1, 141.2, 153.2, 155.4, 177.7. IR (KBr) ν (cm^{-1}) 1669, 1551, 1327, 1031, 770. MS-EI *m/z* (rel. intensity) 318 (85, M^+), 290 (78, $[M - CO]^+$), 262 (41, $[M - 2CO]^+$), 233 (66), 205 (100). HRMS-EI (*m/z*) calcd for $C_{18}H_{10}N_2O_4$ 318.0641, found 318.0650.

2,3-Bis(5-hydroxymethyl-2-furyl)quinoxaline (6). Dialdehyde **5** (15.9 g, 50 mmol) was suspended in methanol (150 mL), and while cooling in an ice bath, $NaBH_4$ (5.67 g, 150 mmol) was added in small portions over a period of 1 h. After the addition was complete, the reaction mixture was stirred for 2 h at 20 °C. TLC indicated the absence of any aldehyde (plate developed with 2,4-dinitrophenylhydrazine). To destroy the excess borohydride in the reaction mixture, glacial acetic acid (10 mL) was added; after stirring for 10 min at 20 °C, the suspension was poured into a cold solution of an excess of $NaHCO_3$ in water (500 mL). The yellow precipitate was collected on a Büchner funnel, washed with water, and dried under vacuum to give the diol **6** (15.3 g, 95%), mp 179 °C. ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 4.56 (s, 4H), 6.52 (d, *J* = 3.4 Hz, 2H), 6.78 (d, *J* = 3.4 Hz, 2H), 7.81 (dd, *J* = 6.4, 3.4 Hz, 2H), 8.06 (dd, *J* = 6.4, 3.4 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 57.5, 110.6, 115.1, 129.7, 131.9, 141.7, 143.9, 151.7, 158.4. IR (KBr) ν (cm^{-1}) 3384, 2486, 2408, 1534, 1386, 1336, 1206, 1089, 1071, 1017, 928, 804, 761. MS-EI *m/z* (rel. intensity) 322 (100, M^+), 304 (99, $[M - H_2O]^+$). HRMS-EI (*m/z*) calcd for $C_{18}H_{14}N_2O_4$ 322.0954, found 322.0955.

2,3-Bis(5-acetoxymethyl-2-furyl)quinoxaline (1f). Diol **6** (11.5 g, 35.4 mmol) was suspended in CH_2Cl_2 (300 mL) and cooled in an ice bath to 0 °C, and then 4-*N*,*N*-dimethylaminopyridine (100 mg) and triethylamine (19.5 mL, 140 mmol) were added. Acetic anhydride (10.0 mL, 105 mmol) was added dropwise, and then the resulting solution was stirred at 20 °C for 15 h. Saturated aqueous $NaHCO_3$ (300 mL) was added, and the mixture was stirred until the evolution of gas stopped; this step, used to quench the excess of acetic anhydride, took up to 1 h. The two layers were separated, and the aqueous phase was extracted with CH_2Cl_2. The combined organic phases were washed ($NaHCO_3$ solution), dried ($MgSO_4$), and filtered. After evaporation of the solvent, the residual solid was treated with diethyl ether (20 mL); the suspension was stirred for 2 min and then diluted with hexanes (100 mL). The white solid was collected on a Büchner funnel, washed with hexanes, and dried under vacuum to give the diacetate **1f** (11.2 g, 78%), mp 125 °C. ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 2.09 (s, 6H), 5.11 (s, 4H), 6.57 (d, *J* = 3.4 Hz, 2H), 6.73 (d, *J* = 3.4 Hz, 2H), 7.76 (dd, *J* = 6.4, 3.4 Hz, 2H), 8.12 (dd, *J* = 6.4, 3.4 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 20.8, 58.0, 112.5, 113.6, 129.1, 130.5, 140.6, 142.3, 151.2, 151.3, 170.4. IR (KBr) ν (cm^{-1}) 3117, 1735, 1378, 1244, 1219, 1026, 950, 814, 770. MS-FAB *m/z* (rel. intensity) 407 (100, MH^+), 347 (31, $[M - Ac]^+$). HRMS-FAB (*m/z*) MH^+ calcd for $C_{22}H_{19}N_2O_6$ 407.1243, found 407.1249.

2,3-Bis(8-acetoxymethyl-11-oxatricyclo[6,2,1,$0^{2,7}$]undeca-2,4,6,9-tetraen-1-yl)quinoxaline (2f). Compound **2f** was prepared according to general procedure A using 7.20 g (52 mmol) of anthranilic acid, 13 mL (0.1 mol) of isoamyl nitrite, and 5.28 g (13 mmol) of the bisacetate **1f**. Column chromatography (CH_2Cl_2/EtOAc, 9:1) provided the adduct **2f** (4.70 g, 65%) as a 6:1 mixture of diastereomers of a white solid. Spectral data for the major isomer: ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 2.02 (s, 6H), 4.73 (d, *J* = 12.5 Hz, 2H), 4.96 (d, *J* = 12.5 Hz, 2H), 6.83 (d, *J* = 5.3 Hz, 2H), 6.91 (br dt, *J* = 7.3, 0.9 Hz, 2H), 7.00 (br dt, *J* = 7.3, 0.9 Hz, 2H), 7.07 (d, *J* = 7.3 Hz, 2H), 7.18 (d, *J* = 7.3 Hz, 2H), 7.38 (d, *J* = 5.3 Hz, 2H), 7.84 (dd, *J* = 6.4, 3.4 Hz, 2H), 8.28 (dd, *J* = 6.4, 3.4 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 20.7, 61.2, 90.3, 94.1, 118.9, 121.7, 124.9, 125.2, 129.4, 130.6, 140.6, 140.7, 147.1, 147.6, 148.3, 152.2, 170.8. IR (KBr) ν (cm^{-1}) 3081, 3025, 2949, 1743, 1453, 1369, 1239, 1044, 758, 699. MS-FAB *m/z* (rel. intensity) 559 (43, MH^+), 499 (20, $[M - OAc]^+$), 487 (26). HRMS-FAB (*m/z*) MH^+ calcd for $C_{34}H_{27}N_2O_6$, 559.1869, found 559.1861.

2,3-Bis(8-hydroxymethyl-11-oxatricyclo[6,2,1,$0^{2,7}$]undeca-2,4,6,9-tetraen-1-yl)quinoxaline (2g). Diacetate **2f** (4.0 g, 7.2 mmol) was suspended in MeOH (100 mL). While stirring at 20 °C, lithium hydroxide monohydrate (890 mg, 21.6 mmol) was added together with water (20 mL). After 15 h at 20 °C, the reaction mixture was diluted with water (150 mL), and the resulting mixture was extracted with EtOAc. The organic extracts were dried (sodium sulfate). After filtration and evaporation of the solvent, the residual oil was taken up in THF (50 mL). This solvent was evaporated again to give diol **2g** (3.16 g, 93%) as a 6:1 mixture of isomers of a slightly yellow solid. Spectral data for the major isomer in the diastereomeric mixture: ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 4.31 (d, *J* = 12.7 Hz, 2H), 4.38 (d, *J* = 12.7 Hz, 2H), 6.87−6.93 (m, 4H), 7.00 (br dt, *J* = 7.3, 0.9 Hz, 2H), 7.11 (d, *J* = 7.3 Hz, 2H), 7.18 (d, *J* = 7.3 Hz, 2H), 7.39 (d, *J* = 5.28 Hz, 2H), 7.84 (dd, *J* = 6.3, 3.5 Hz, 2H), 8.27 (dd, *J* = 6.3, 3.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 60.2, 93.3, 93.7, 119.2, 121.2, 124.6, 125.3, 129.2, 130.7, 140.5, 141.2, 147.1, 147.8, 148.5, 152.8. IR (KBr) ν (cm^{-1}) 3429, 3066, 2926, 1453, 1042, 761, 693. MS-EI *m/z* (rel. intensity) 474 (12, M^+), 444 (24, $[M - CH_2O]^+$), 427 (35), 415 (53), 385 (65), 301 (100). HRMS-EI (*m/z*) calcd for $C_{30}H_{22}N_2O_4$, 474.1580, found 474.1585.

2,3-Bis(8-allyloxymethyl-11-oxatricyclo[6,2,1,$0^{2,7}$]undeca-2,4,6,9-tetraen-1-yl)quinoxaline (2h). Allyl bromide (0.251 g, 2.11 mmol) was added to a solution of diol **2g** (0.202 g, 0.422 mmol) and NaH (0.343 g, 4.22 mmol) in dry THF (20 mL) under Ar. The resulting solution was stirred vigorously for 18 h until all of the starting materials had been consumed (TLC). Saturated NH_4Cl solution (50 mL) was added, and the mixture was extracted with CH_2Cl_2. The organic layer was dried (Na_2SO_4), filtered, concentrated, and then passed through a plug of silica gel using CH_2Cl_2 as eluent. After the obtained solution was dried (Na_2SO_4) and the solvent was evaporated, a yellow oil (181 mg, 77%) was obtained. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 3.76−3.78 (m, 4H), 4.06 (d, *J* = 11.5 Hz, 2H), 4.13 (d, *J* = 11.5 Hz, 2H), 4.96−5.06 (m, 4H), 5.60−5.72 (m, 2H), 6.76−6.79 (m, 2H), 6.83−6.85 (m, 2H), 6.91−6.93 (m, 2H), 7.12−7.14 (m, 2H), 7.27 (d, *J* = 5.3 Hz, 2H), 7.65 (dd, *J* = 6.5, 3.4 Hz, 2H), 8.15 (dd, *J* = 6.5, 3.4 Hz, 2H). ^{13}C NMR

(100 MHz, $CDCl_3$) δ (ppm) 67.0, 72.2, 91.6, 93.8, 116.6, 119.1, 121.1, 124.4, 129.1, 130.2, 134.4, 140.3, 141.4, 146.8, 147.8, 148.4, 152.3. FT-IR (KBr) ν (cm^{-1}) 541, 651, 694, 733, 763, 929, 995, 1055, 1098, 1267, 1364, 1454, 1479, 1561,2856, 3068. HRMS-EI (*m*/*z*) calcd for $C_{36}H_{30}N_2O_4$, 554.2206, found 554.2213.

General Procedure B. Bis(isobenzofuran) Additions to C_{60} To Give Adducts 4e and 4e−j. The bis(isobenzofuran) precursor (**2a**−**k**; 1 equiv relative to C_{60}) and a tetrazine (**3a** or **3b**; 2.2 equiv relative to **2a**−**k**) were added to a solution of C_{60} in freshly distilled toluene (1−1.5 mg C_{60}/mL toluene) at 20 °C. This reaction mixture was then stirred under Ar for 4 h at either 45 °C (when **3a** was used) or 25 °C (when **3b** was used). The resulting brown solution was then evaporated and subjected to flash chromatography (toluene/EtOAc, 9:1). The purple fraction containing unreacted C_{60} eluted first, followed by the fraction containing the desired *cis-1* adduct (**4b** and **4e**−**j**), which was then concentrated. The residual brown solid was redissolved in an appropriate solvent (e.g., CS_2 or $CHCl_3$; 1 or 2 mL). This solution was then added to stirred pentane (20−30 mL) to precipitate the products. Finally, the slurry was centrifuged, and the resulting solid collected and dried under vacuum. See experimental description and spectral data for compounds **4f**−**k** in Supporting Information.

anti/syn-**9,10-(1-(1′-(11′-Oxaticyclo[6.2.1.0^{2,7}]undeca-2′,4′,6′,9′-tetraenylmethyl))-11-oxatricyclo[6.2.1.0^{2,7}]undeca-2,4,6-trieno)-1″,2″-buckminsterfullerene (4b′) and 9,10,10′,9′-(Bis-1,1′-(11-oxatricyclo[6.2.1.0^{2,7}]undeca-2,4,6-trieno)methane)-1″,2″,3″,4″-buckminsterfullerene (4b).** A solution of the benzyne bisfuran adduct **2b** (156 mg, 0.52 mmol) and 3,6-bis(2-pyridyl)tetrazine **3a** (270 mg, 1.14 mmol) was stirred with C_{60} (288 mg, 0.4 mmol) for 20 h at 45 °C. The solvent was evaporated under reduced pressure. Just enough hexanes was added to avoid precipitation, followed by immediate loading on a silica gel column for purification. Flash chromatography (SiO_2, toluene/hexanes, 1:1) gave unreacted C_{60} and two fractions containing the C_{60} adducts. The first fraction contained the monoadduct **4b′** (11 mg, 2.8%; 3.2% based on recovered C_{60}), which was isolated as a brown solid. Spectral data for compound **4b′**: ^1H NMR (500 MHz, $CS_2/CDCl_3$, 9:1) δ (ppm) 3.96 (d, J = 15.7 Hz, 1H), 4.03 (d, J = 15.7 Hz, 1H), 5.49 (s, 1H), 6.72 (m, 1H), 6.78 (s, 1H), 6.86−6.96 (m, 4H), 7.03−7.04 (m, 1H), 7.10−7.13 (m, 1H), 7.35−7.43 (m, 3H), 7.56−7.57 (m, 1H), 7.71−7.73 (m, 1H). ^{13}C NMR (125.7 Hz, $CS_2/CDCl_3$, 9:1) δ (ppm) 32.1, 77.8, 80.4, 81.2, 88.3, 90.0, 96.3, 119.1, 119.4, 121.0, 124.2, 124.45, 124.51, 125.1, 127.2, 127.3, 127.9, 128.7, 137.0, 137.3, 137.4, 137.7, 137.8, 139.4, 139.47, 139.54, 139.9, 141.3, 141.4, 141.5, 141.6, 141.65, 141.69, 141.74, 141.77, 141.82, 141.9, 142.1, 142.2, 142.30, 142.33, 142.4, 143.2, 143.75, 143.79, 144.1, 144.17, 144.23, 144.3, 144.79, 144.82, 144.83, 144.89, 144.93, 145.0, 145.11, 145.14, 145.47, 145.49, 145.58, 145.63, 145.64, 145.67, 145.74, 145.76, 145.80, 145.9, 146.0, 146.6. FT-IR (KBr) ν (cm^{-1}) 1650, 1638, 1385, 1182, 747, 527.

The second fraction contained the bisadducts **4b**. Yield: 193 mg, 50% (57% based on recovered C_{60}) as a brown solid. ^1H NMR (500 MHz, $CS_2/CDCl_3$, 5:1) δ (ppm) 3.73 (d, J = 14.8 Hz, 1H), 3.94 (d, J = 14.8 Hz, 1H), 6.70 (s, 2H), 7.34−7.36 (m, 4H), 7.43−7.45 (m, 2H), 7.51−7.54 (m, 2H). ^{13}C NMR (125.7 Hz, CS_2/$CDCl_3$, 5:1) δ (ppm) 28.5, 73.6, 77.9, 88.2, 102.5, 120.0, 123.7, 127.2, 127.4, 136.4, 137.4, 138.5, 140.4, 141.5, 142.0, 142.5, 142.6, 142.9, 143.0, 143.1, 143.2, 143.7, 143.8, 143.92, 143.94, 144.0, 144.7, 144.8, 145.0, 145.2, 145.3, 145.8, 146.1, 146.4, 146. 8, 147.0, 147.9, 148.1, 149.0, 149.5, 154.7. FT-IR (KBr) ν (cm^{-1}) 2966, 2923, 2851, 1650, 1638, 1459, 752, 525. FAB-MS: *m*/*z* (rel. intensity) 969 (5, MH^+), 720 (15). HRMS (*m*/*z*) calcd for $C_{77}H_{13}O_2$ ($M + H^+$) 969.0916, found 969.0950.

cis-1 **Bis(isobenzofuran)-C_{60} Adduct 4e.** Compound **4e** was prepared according to general procedure B described above using 144 mg (0.2 mmol) of C_{60}, 82.9 mg (0.2 mmol) of quinoxaline **2e**, and 0.2 mL (0.6 mmol) of a 3 M solution of the parent tetrazine **3b** in CH_2Cl_2. After column chromatography and eluting with toluene/ethyl acetate 9:1 (R_f = 0.70), the cycloadduct was obtained as a brown solid to give 78 mg of **4e** (36%; 47% based on recovered C_{60}). ^1H NMR (500 MHz, $CDCl_3/CS_2$, 3:1) δ (ppm) 6.73 (s, 2H), 7.31−7.38 (m, 4H), 7.44 (d, J = 7.1 Hz, 2H), 7.90−7.93 (m, 4H), 8.30 (dd, J = 6.4, 3.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3/CS_2$ 3:1) δ (ppm) 72.8, 77.5, 88.5, 94.7, 119.8, 126.2, 127.0, 129.1, 129.7, 131.1, 135.1, 136.1, 138.5, 140.0, 140.1, 141.0, 141.3, 141.7, 142.13, 142.14, 142.3, 142.4, 142.7, 143.2, 143.35, 143.43, 143.5, 143.6, 143.7, 143.9, 144.2, 144.3, 144.7, 144.8, 145.58, 145.60, 146.0, 146.5, 146.8, 147.56, 147.61, 148.5, 148.6, 150.2, 151.6. IR (KBr) ν(cm^{-1}) 1686, 1462, 1384, 1348, 1192, 1103, 1058, 1016, 957, 917, 751, 689, 525. MS-FAB *m*/*z* (rel. intensity) 1084 (22, MH^+), 720 (100, C_{60}^+). HRMS-FAB (*m*/*z*) MH^+ calcd for $C_{84}H_{15}N_2O_2$ 1083.1133, found 1083.1180.

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Supporting Information Available: Spectral data of new compounds, crystallographic information files in CIF format, and Cartesian coordinates of optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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