Reversible Diels−Alder Addition to Fullerenes: A Study of Equilibria Using ^{3}He NMR Spectroscopy

Guan-Wu Wang,† Martin Saunders,* and R. James Cross*

Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06520-8107

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Abstract: ^{3}He NMR spectroscopy has been used to study the equilibria of Diels−Alder additions of 9,10-dimethyl anthracene (DMA) to ^{3}He@C_{60} and ^{3}He@C_{70}. Spectra of a series of equilibrium mixtures showed peaks for the isomeric adducts. One monoadduct, six bis-adducts, eleven tris-adducts, and ten tetrakis-adducts of DMA to C_{60} were seen. One monoadduct and three bis-adducts of C_{70} were detected. Equilibrium constants were found for these reactions and values for ΔG, ΔH, and ΔS were obtained.

Introduction

C_{60} and other fullerenes are quite reactive.[1−3] Most reactions result in irreversible addition to yield mixtures of mono- and multiple adducts. However, the Diels−Alder reaction of 9,10-dimethylanthracene (DMA) with C_{60} (see Figure 1) has been shown by Hirsch et al. to be **reversible** at room temperature, yielding mixtures of isomers of $C_{60}(DMA)_n$.[4] DMA behaves in a similar manner toward C_{70}. These reactions are of interest because the equilibrium quantities of the regioisomers can yield thermodynamic information about these compounds. How can one study these equilibria? We have shown that ^{3}He NMR is a very powerful tool for studying fullerene reactions.[5,6] Each ^{3}He-labeled fullerene and fullerene derivative gives a distinct, sharp ^{3}He NMR peak. In this paper, we report the use of ^{3}He NMR to determine the number of addends, equilibrium constants, ΔG, ΔH, and ΔS for $C_{60}(DMA)_n$ and $C_{70}(DMA)_n$. We believe that ^{3}He inside fullerenes has a negligible effect on rates and equilibrium constants for reactions. In all cases where the same reactions have been studied using ^{3}He NMR and using other methods, the same results have been obtained.

With reactions that add across 6,6 fusions, only one monoadduct of C_{60} is formed. There are eight possible regioisomers for bis-addition of a symmetric addend, and there is a case[7] where all of them have been separated and characterized. Nine regioisomers[8] of C_{60} bis-adducts have been separated when the second addend is different from the first. Separation of the individual isomers of tris- and higher adducts is difficult. Characterization of only a few of them[9,10] have been reported. Recently Hirsch's group has isolated seven regioisomers[11] out

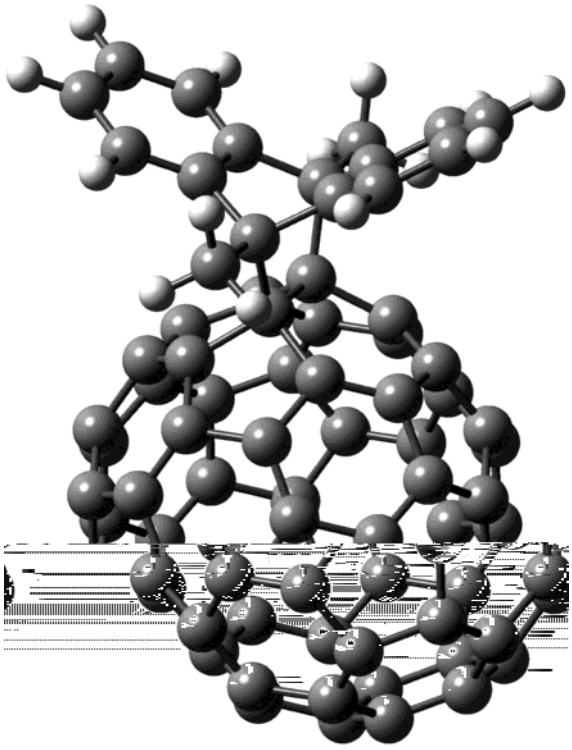

Figure 1. The monoadduct of 9,10-dimethylanthracene and C_{60}. The figure was made using GaussView 2.1.

† Present address: Dept. of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China.

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of 46 possible tris-adducts of Bingel reaction products of C_{60}. The chemistry of C_{70} is potentially more complex than that of C_{60} due to the lower symmetry of C_{70}. Four monoadducts from the reaction mixture of C_{70} and benzyne have been separated,[12] and some examples of bis- up to octakis-adducts have been reported.[3,13] However, the determination of the maximum number of the tris-adducts and higher adduct isomers of C_{60} and C_{70} formed in a reaction remains a challenging task.

Experimental Section

^{3}He-labeled fullerenes were prepared by using our high-temperature and high-pressure procedure.[14] C_{60} and C_{70} were labeled with ^{3}He six times and twice, respectively, to get more ^{3}He into the cages of fullerenes and thus obtain much better signal-to-noise ratios in the ^{3}He NMR spectra. All ^{3}He NMR samples were prepared directly in NMR tubes. A weighed amount of DMA and ^{3}He@C_{60} (7.20 mg) or ^{3}He@C_{70} (4.20 mg) and 1 mg of Cr(acac)$_3$ were put in a NMR tube and dissolved in 4:1 1-methylnaphthalene/CD_2Cl_2 (0.4 mL). First, 0.5 equiv of DMA was added. The mixture was allowed to stand long enough (overnight)[15] to reach the equilibrium, and its ^{3}He NMR spectrum was taken. Then a weighed amount of DMA was added to the above mixture to get another sample. This procedure could be repeated many times until a saturated solution was reached. About 15 equiv of DMA can be added to ^{3}He@C_{60} and 1 equiv of DMA to ^{3}He@C_{70} with no precipitation. For the variable-temperature experiments, the samples were equilibrated for at least 1 h in the probe before an acquisition was started. A mixture of 3.60 mg ^{3}He@C_{60}, 4.20 mg of ^{3}He@C_{70}, 1.55 mg of DMA (0.75 equiv), and 1 mg of Cr(acac)$_3$ was prepared in 0.4 mL of 4:1 1-methylnaphthalene/CD_2Cl_2 to get the ratio of the equilibrium constants for C_{60} with DMA versus C_{70} with DMA from the ^{3}He NMR. All ^{3}He NMR spectra were taken at 381 MHz on a Bruker AM-500 NMR spectrometer with ^{3}He dissolved in the solution as reference. No pulse delay was used, and a line-broadening of 2 Hz was applied.

Results and Discussion

The Diels−Alder addition of DMA to C_{60} is reversible at ambient temperatures, and gives, successively, mono-, bis-, tris-, and tetrakis-adducts with increasing DMA concentration. As more DMA is added, larger amounts of higher adducts are formed. A series of mixtures of DMA and ^{3}He@C_{60} was prepared in 4:1 1-methylnaphthalene/CD_2Cl_2. After the equilibrium was established, the ^{3}He NMR spectra were recorded. With few exceptions, each line in the ^{3}He NMR spectra is well resolved and corresponds to a distinct fullerene adduct. Two representative ^{3}He NMR spectra of ^{3}He@C_{60} with 2.5 equiv and 10 equiv of DMA are shown in Figure 2.

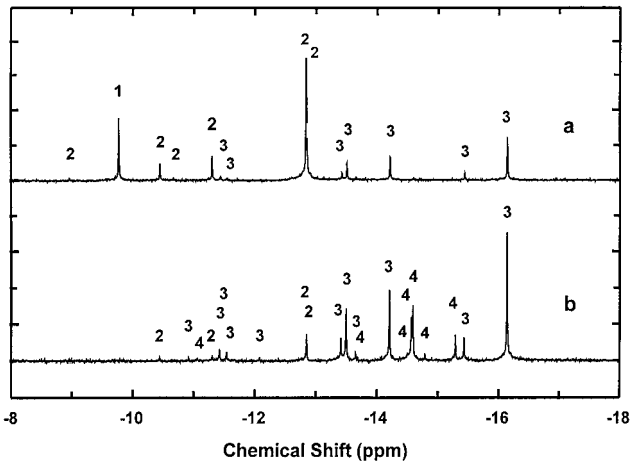

Figure 2. ^{3}He NMR spectra of ^{3}He@C_{60} with (a) 2.5 equiv of DMA and (b) 10 equiv of DMA at room temperature. The numbers **1**, **2**, **3**, **4** stand for the isomers of mono-, bis-, tris-, and tetrakis-adducts, respectively.

Table 1. Chemical Shifts and Fractional Concentrations for the Reaction of C_{60} and DMA at 295.4 K

	δ^a	F^b		δ^a	F^b
	Mono			Tetrakis	
	−9.77	1.000	1	−11.08	0.012
	Bis		2	−12.77	0.011
1	−8.95	0.006	3	−13.70	0.026
2	−10.44	0.060	4	−14.52	0.045
3	−10.66	0.008	5	−14.57	0.280
4	−11.29	0.087	6	−14.60	0.367
5	−12.83	0.448	7	−14.79	0.037
6	−12.84	0.392	8	−15.26	0.027
			9	−15.30	0.168
			10	−15.47	0.027
	Tris				
1	−10.93	0.008			
2	−11.42	0.014			
3	−11.43	0.028			
4	−11.54	0.021			
5	−12.08	0.008			
6	−13.42	0.068			
7	−13.50	0.157			
8	−13.65	0.020			
9	−14.21	0.217			
10	−15.44	0.067			
11	−16.14	0.390			

^{a} Chemical shift in ppm relative to dissolved ^{3}He gas. ^{b} Fraction in each isomer of the total NMR signal for all isomers with a given number of DMA addends.

The assignment of a given NMR peak to the number of DMA addends is straightforward. If the ratio of NMR intensities of two peaks is independent of DMA concentration, then the two peaks correspond to adducts with the same number of DMA molecules. If the ratio changes with DMA concentration, the peak that increases more rapidly corresponds to an adduct with more DMA molecules. The 29 distinct ^{3}He peaks seen were assigned in this way. We found one monoadduct, six bis-adducts, eleven tris-adducts, and ten tetrakis-adducts. We have seen no evidence of pentakis- or hexakis-adducts even at the highest concentrations of DMA available to us. The amount of any single higher adduct is evidently too low for us to detect. Table 1 lists the isomers, their ^{3}He NMR shifts, and the fraction of the NMR intensity for each isomer at 295.4 K. Figure 3 shows distributions of C_{60}, monoadduct, and the

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(15) 7.20 mg of C_{60} and 2.06 mg of DMA (1 equiv) were mixed in 0.5 mL of ODCB-d_4. ^{1}H NMR was used to follow the reaction of C_{60} and DMA. It was found that almost no free DMA could be found by ^{1}H NMR 30 min. after the mixing.

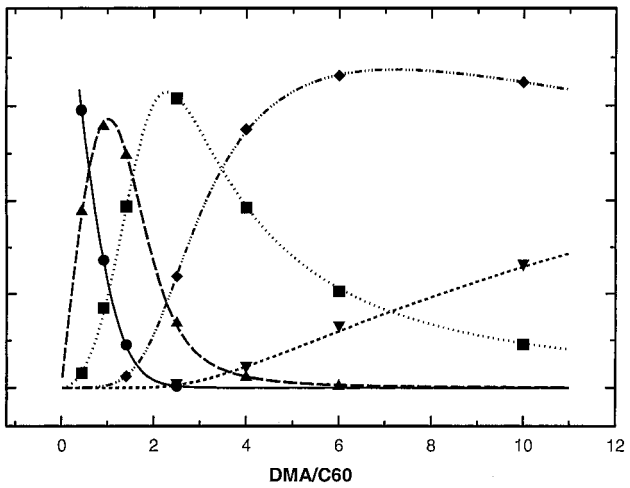

Figure 3. Distributions of C_{60} and $C_{60}(DMA)_n$ at different ratios of DMA/C_{60}. (●) C_{60}; (▲) monoadduct; (■) bis-adducts; (◆) tris-adducts; (▼) tetrakis-adducts. The curves (——) C_{60}; (− − −) monoadduct; (···) bis-adducts; (-···-··-···) tris-adducts; (- - -) tetrakis-adducts) are the calculated curves by inputting the K_1, K_2, K_3, K_4 as 3634, 496, 41.7, 2.36 M^{-1}, and the concentration of C_{60} as 0.025M.

sums of bis-, tris- and tetrakis-addducts at different ratios of DMA/C_{60}.

We assumed the reversible reactions of $^3He@C_{60}$ and DMA as shown in eqs 1−4:

$$^3He@C_{60} + DMA \overset{K_1}{\rightleftharpoons} {}^3He@C_{60}(DMA) \quad (1)$$

$$^3He@C_{60}(DMA) + DMA \overset{K_2}{\rightleftharpoons} {}^3He@C_{60}(DMA)_2 \quad (2)$$

$$^3He@C_{60}(DMA)_2 + DMA \overset{K_3}{\rightleftharpoons} {}^3He@C_{60}(DMA)_3 \quad (3)$$

$$^3He@C_{60}(DMA)_3 + DMA \overset{K_4}{\rightleftharpoons} {}^3He@C_{60}(DMA)_4 \quad (4)$$

The quantities considered in these equations are the sums of all bis-, tris- and tetrakis-adducts. While the relative amounts of C_{60} and the mono-, bis-, tris- and tetrakis-adducts are observable by using the ^3He spectra, the amount of free DMA is not directly observable in the ^3He spectrum. Therefore, a computer program was written which uses the concentration of free DMA as a parameter in simulating the experimental results. For any set of assumed values of K_1, K_2, K_3, K_4, a series of values for concentrations of free C_{60} and free DMA was generated. From these values, the sums of the concentrations of the different kinds of adducts could be generated using the above equations. Adding these concentrations generates values for the total concentration of C_{60}. Total DMA was calculated by addition weighted by the number of DMA molecules on each adduct. These calculated values could then be compared with the experimental values. K_1, K_2, K_3, and K_4 were adjusted to fit the experimental points. Values of 3600, 490, 41, 2.3 M^{-1} were found to best fit the experimental data and yielded the theoretical concentration curves shown in Figure 3. As can be seen, all of the experimental points for the fractions of C_{60} and $C_{60}(DMA)_n$ at different DMA/C_{60} ratios are very near to the calculated curves. The concentration of free C_{60} decreases with added DMA and is near zero at 2 equiv of DMA, while those of the mono-, bis- and tris-adducts first increase and reach a maximum and then decrease. The concentration of tris-adduct reaches its maximum at 6 equiv of DMA and then decreases slowly. The concentration of tetrakis-adducts is still going up.

Table 2. Peak Intensities, Equilibrium Constants *K*, and Free Energies ΔG of $C_{60} + n$DMA $\leftrightarrows$ $C_{60}(DMA)_n$[a]

T (K)	295.4	305.0	315.0	325.0
C_{60}	17.66	14.49	6.21	14.30
mono	39.32	26.81	8.83	13.89
bis 2	0.84	0.69		
bis 4	1.09	0.94		
bis 5	5.65	3.65	0.94	1.37
bis 6	4.70	3.21	0.74	0.92
bis total	12.27	8.49	1.68	2.29
$C_{DMA'}$ (mM)[b]	0.617	1.688	5.448	8.526
K_1 (M^{-1})	3600	1100	260	110
K_2 (M^{-1})	510	190	35	19
ΔG_1 (kcal mol^{-1})	−4.8	−4.2	−3.5	−3.1
ΔG_2 (kcal mol^{-1})	−3.7	−3.2	−2.2	−1.9

[a] The initial (unreacted) concentrations are C_{60}: 25.0 mM, DMA: 23.7 mM. [b] The concentration of free DMA obtained by subtracting the amount of bound DMA from the initial concentration.

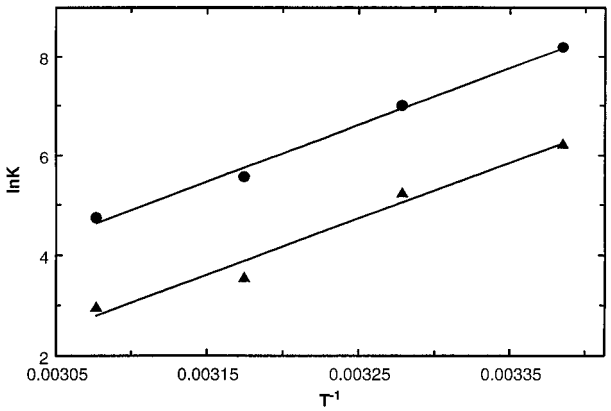

Figure 4. The plots of ln *K* vs T^{-1} for the first two equilibria of the reaction of C_{60} with DMA. (●) K_1; (▲) K_2.

Table 3. Chemical Shifts and Fractional Concentrations for the Reaction of C_{70} and DMA at 295.4 K

	δ[a]	F[b]
	C_{70}	
1	−28.80	1.000
	Mono	
1	−26.93	1.000
	Bis	
1	−24.73	0.389
2	−24.67	0.139
3	−24.59	0.472

[a] Chemical shift in ppm relative to dissolved ^3He gas. [b] Fraction in each isomer of the total NMR signal for all isomers with a given number of DMA addends.

It was also possible to derive equations for obtaining the equilibrium constants directly from the experimental data without using the simulation process described above. Knowing the initial amounts of C_{60} and DMA and the relative amounts of each product, one can calculate the concentration of free DMA by subtracting the concentrations of the adducts. The resulting equilibrium constants were similar to those obtained by the simulation method.

The highest field helium peak of the tris-adducts is shifted further upfield than the highest field peak of the bis-adducts, but the highest field peak of the tetrakis-adducts is not as far upfield. The magnetic field inside the C_{60} cage changes with both the number of added groups and the addition patterns. The

Table 4. Peak Intensities, Equilibrium Constants K, and Free Energies ΔG of $C_{70} + n$DMA $\leftrightarrows$ $C_{70}(DMA)_n$[a]

T (K)	295.4	305.0	315.0	325.0
C_{70}	104.79	304.24	52.30	32.90
mono	59.05	122.41	12.72	4.34
bis 1	1.56	2.34		
bis 2	0.32	0.71		
bis 3	1.83	2.68		
bis total	3.71	5.73		
$C_{DMA'}$ (mM)[b]	0.7539	1.964	3.547	4.645
K_1 (M^{-1})	750	210	69	28
K_2 (M^{-1})	83	24		
ΔG_1 (kcal mol^{-1})	−3.9	−3.2	−2.7	−2.2
ΔG_2 (kcal mol^{-1})	−2.6	−1.9		

[a] The initial (unreacted) concentrations are C_{70}: 13.9 mM, DMA: 6.26 mM. [b] The concentration of free DMA obtained by subtracting the amount of bound DMA from the initial concentration.

number of $C_{60}(DMA)_n$ isomers seen increases from one for the monoadduct, six for the bis-adducts, eleven for tris-adducts and then decreases to ten for tetrakis-adducts. Furthermore, the numbers of major isomers increase first and then decrease, one for monoadduct, four for bis-adducts, four for tris-adducts, and three for tetrakis-adducts. The addition of DMA to C_{60} seems to be more selective at later stages.

Elevated temperature drives the equilibrium back toward free C_{60}. ^{3}He NMR spectra of a fixed amount of ^{3}He@C_{60} and DMA were obtained at different temperatures (from 295.4 to 325 K). These data allow the calculation of the equilibrium constants K and free energies ΔG. Table 2 lists these results along with the peak intensities at different temperatures.

Assuming ΔH does not change over our temperature range (30 °C), applying the van't Hoff equation gives:

$$\frac{d(\ln K)}{d(1/T)} = -\frac{\Delta H}{R} \quad (5)$$

The slope of the graph of ln K vs T^{-1} multiplied by $-R$ gives ΔH. Figure 4 shows the plots of ln K vs T^{-1} for the first two equilibria of the reaction of C_{60} with DMA. A least-squares fit gives ΔH_1 as −22.9 kcal mol^{-1} for C_{60} + DMA $\leftrightarrows$ C_{60}(DMA), and ΔH_2 as −22.5 kcal mol^{-1} for C_{60}(DMA) + DMA $\leftrightarrows$ $C_{60}(DMA)_2$. ΔS can be calculated from

$$\Delta G = \Delta H - T\,\Delta S \quad (6)$$

ΔS_1 and ΔS_2 are −61.2 and −63.7 cal mol^{-1} K^{-1}, respectively.

In the same way, we obtained the number of isomers and equilibrium constants for the reaction of ^{3}He@C_{70} and DMA. Unfortunately, the solubility of $C_{70}(DMA)_n$ is much lower than that of $C_{60}(DMA)_n$. When the DMA concentration is higher than 1.5 equivalent in 14 mM C_{70}, $C_{70}(DMA)_n$ started to precipitate out. We found only one monoadduct[16] and three bis-adducts in the equilibrium reaction mixtures. The chemical shifts and equilibrium fractions are given in Table 3. The equilibrium constants and ΔGs are listed in Table 4.

(16) Besides ^{3}He@C_{70}(DMA), the dihelium species $^3He_2$@C_{70}(DMA) was also observed at −26.77 ppm. Its intensity is 10% of ^{3}He@C_{70}(DMA) and the chemical difference is 52 Hz. For a similar observation, see: Khong, A.; Jiménez-Vázquez, H. A.; Saunders, M.; Cross, R. J.; Laskin, J.; Peres, T.; Lifshitz, C.; Strongin, R.; Smith, A. B., III. *J. Am. Chem. Soc*. **1998**, *120*, 6380−6383.

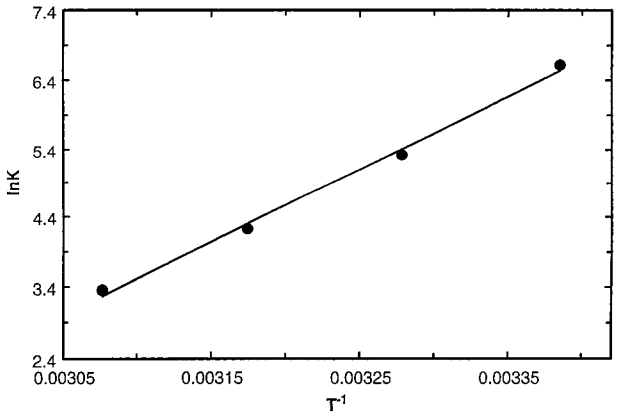

Figure 5. The plot of ln K_1 vs T^{-1} for the first equilibrium of the reaction of C_{70} with DMA.

The plot of ln K_1 vs T^{-1} for C_{70} + DMA $\leftrightarrows$ C_{70}(DMA) is shown in Figure 5. The same treatment as for C_{60} gives ΔH_1 and ΔS_1 as −21.1 kcal mol^{-1} and −58.5 cal mol^{-1} K^{-1}. ΔH_1 and ΔS_1 values for the reaction of C_{70} with DMA are very close to those of ΔH_1 and ΔS_1 and ΔH_2 and ΔS_2 for the reaction of C_{60} and DMA. This is reasonable because both C_{60} and C_{70} involve same type of reacting double bond and same reagent DMA in the Diels−Alder reactions.

We have also run the ^{3}He NMR spectrum of a mixture of ^{3}He@C_{60}, ^{3}He@C_{70}, and DMA to determine the relative equilibrium constants. The ratio $K_1(C_{60})/K_1(C_{70})$ of the first equilibrium for the reactions of DMA with C_{60} and C_{70} is

K_1(C$_{6\ 0\ Ta4\ 40h317\ Tm\ (6\ 0\ Ta486\ 0\ Ta486\ 0\ Ta0)Tj\ 2o73\ m\ 37j\ 6.684\ \ 2o73\ 9\ m\ 294.034\ 59}$

The ratio $K_1(C_{60})/K_1(C_{70})$ is 4.65, very close to the ratio of 4.83 (3608 M^{-1}/747 M^{-1}) obtained from the separate experiments.

We have tried to react ^{3}He@C_{60} with 9,10-diphenylanthracene (DPA), but only the sharp peak of ^{3}He@C_{60} could be observed after an overnight ^{3}He NMR run. The reaction of DPA with C_{60} seems to be much less favorable. Studies on the reactions of fullerenes with other anthracene derivatives are underway.

Conclusions

We have utilized ^{3}He NMR spectroscopy to study the equilibria of the reactions of C_{60} and C_{70} with DMA. By collecting a series of ^{3}He NMR spectra of reaction mixtures of ^{3}He@C_{60} and ^{3}He@C_{70} and DMA, we are able to determine the number of DMA residues bound to the fullerene for each peak in the ^{3}He NMR spectra and to identify how many isomers exist in the reaction mixtures. We found one monoadduct, six bis-adducts, eleven tris-adducts, and ten tetrakis-adducts of $C_{60}(DMA)_n$, and one monoadduct, three bis-adducts of $C_{70}(DMA)_n$ in the equilibrated reaction mixtures. We obtained equilibrium constants for the reactions of C_{60} and C_{70} with DMA and the associated ΔG, ΔH, and ΔS values.

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