Supporting Information

Title: Reducing ability of supramolecular C_{60} dianion toward C=O, C=C and N–N bonds

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1. MOZYME (AM1) analysis on structure of γ-cyclodextrin-bicapped C_{60}·$16H_2O$.

2. FAB-MS data of γ-cyclodextrin-bicapped C_{60} (**1**).

3. Experimental data on efficiency of **2** in ketone reduction: Ketone was reacted with **2** (generated from **1** and $NaBH_4$) in DMSO - H_2O (9:1, v/v) at 25 °C for 1 h. The reaction mixture was diluted with water and extracted with diethyl ether (twice). The ether layer was washed with water and dried over $MgSO_4$. The control experiment was made by using $NaBH_4$ instead of **2** under the same condition. The product (GC-MS) and yield (GLC) are shown in the Table.

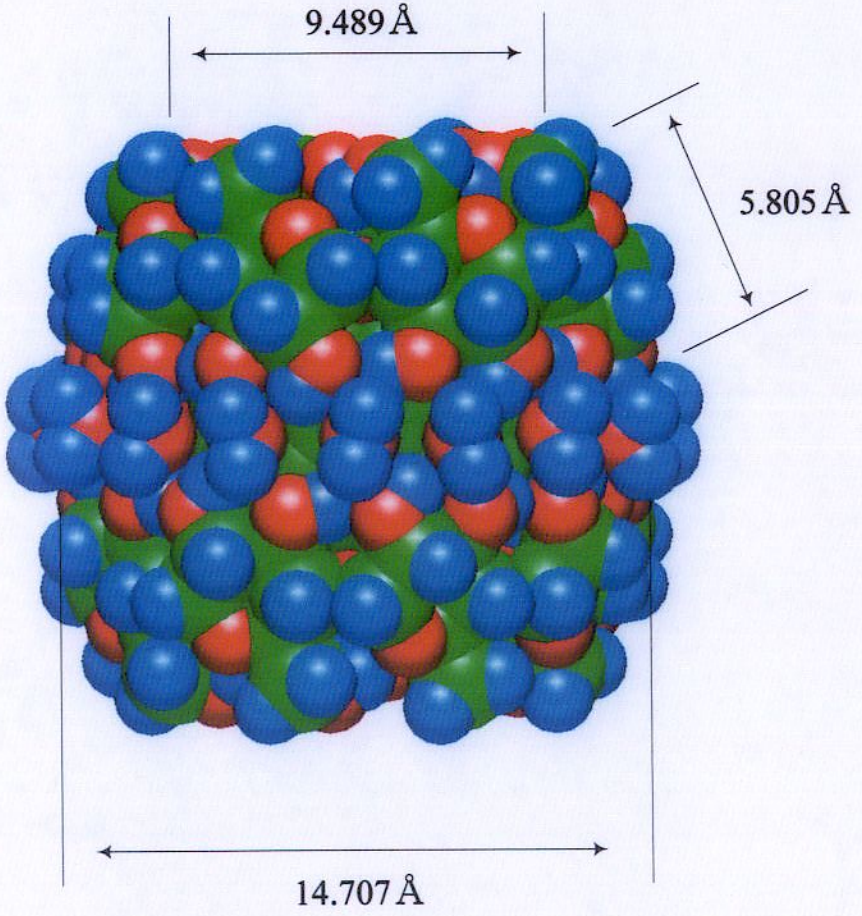
Heat of Formation, Heat of Complexation, and HOMO LUMO Obtained by MOZYME (AM1) Calculation

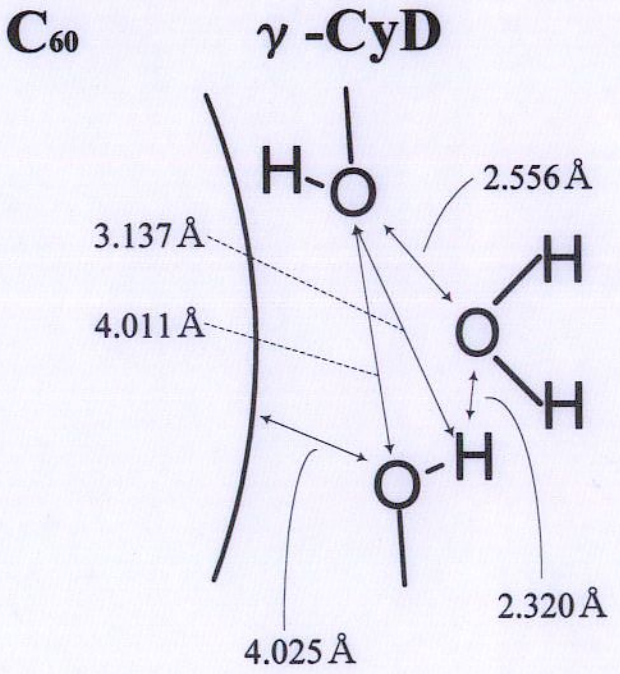
KEYWORD : BFGS PRECISE GEO-OK AM1 ALLBONDS SCFCRT=10^{-10} PL
EIGEN VECTORS ALLVEC T=11D

	Heat of Formation (kcal/mol)	Gradient Norm	HOMO (eV)	LUMO (eV)	HOMO-LUMO gap (eV)	next LUMO (eV)
H_2O	**-59.247**	**1.317**				
γ-CyD	**-1667.737**	**7.880**				
C_{60}	**973.004**	**63.002**	**-9.6204**	**-2.9681**	**6.6523**	
C_{60} / γ-CyD	**-893.955**	**863.693**	**-9.6827**	**-3.0213**	**6.6614**	**-2.3312**
Bicapped C_{60}	**-2768.469**	**255.948**	**-9.5630**	**-3.0334**	**6.5296**	**-2.3128**
Bicapped $C_{60}\cdot 16H_2O$	**-3760.248**	**421.820**	**-8.8907**	**-2.2829**	**6.6078**	**-1.5801**

Complex	ΔH_f (kcal/mol)	$\Sigma \Delta H_f$ (kcal/mol)	$-\Delta H_{complex}$ (kcal/mol)	
C_{60} / γ-CyD	**-893.955**	**-694.73**	**199.22**	**Stabilization**
Bicapped C_{60}	**-2768.469**	**-2362.47**	**406.00**	**Stabilization**
Bicapped $C_{60}\cdot 16H_2O$	**-3760.248**	**-3310.42**	**449.83**	**Stabilization**

MOZYME analysis on structure of γ -cyclodextrin-bicapped $C_{60} \cdot 16H_2O$



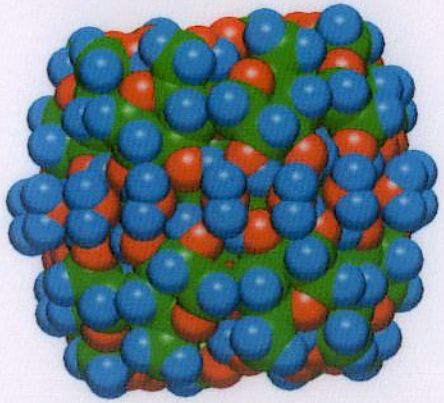


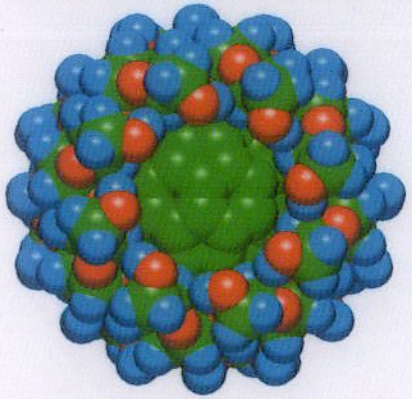
【 Space Filling 】

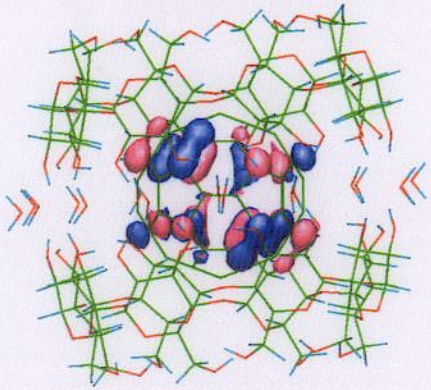
【 HOMO 】

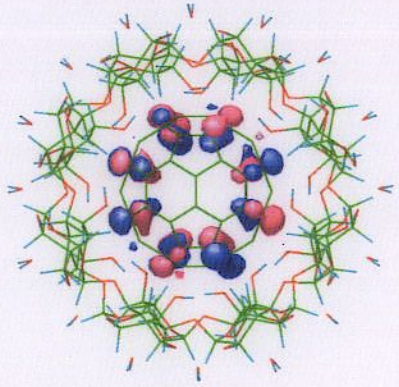
【 LUMO 】

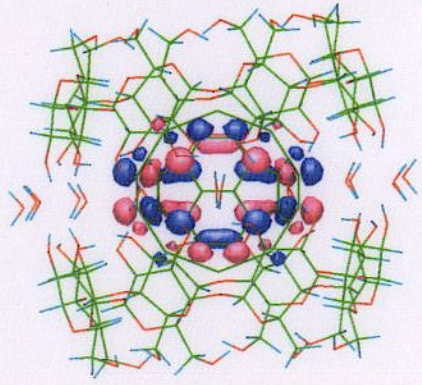
【 next LUMO 】

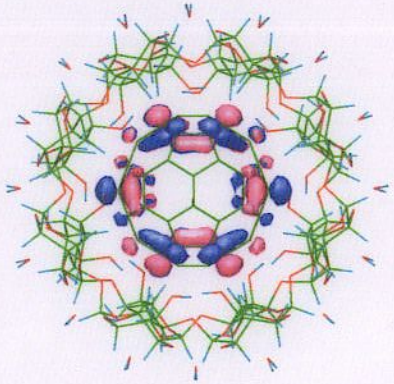


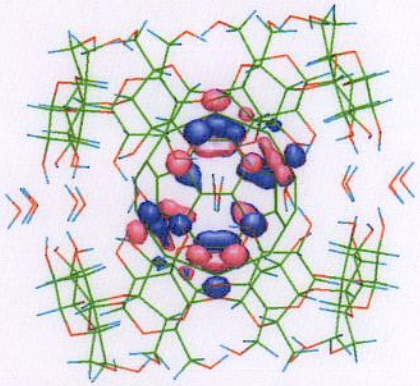


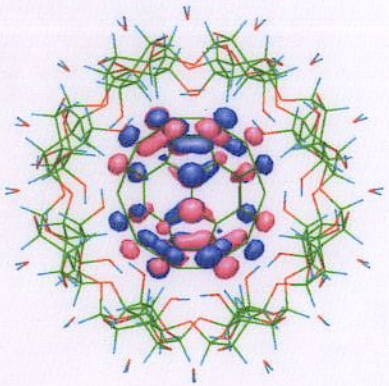










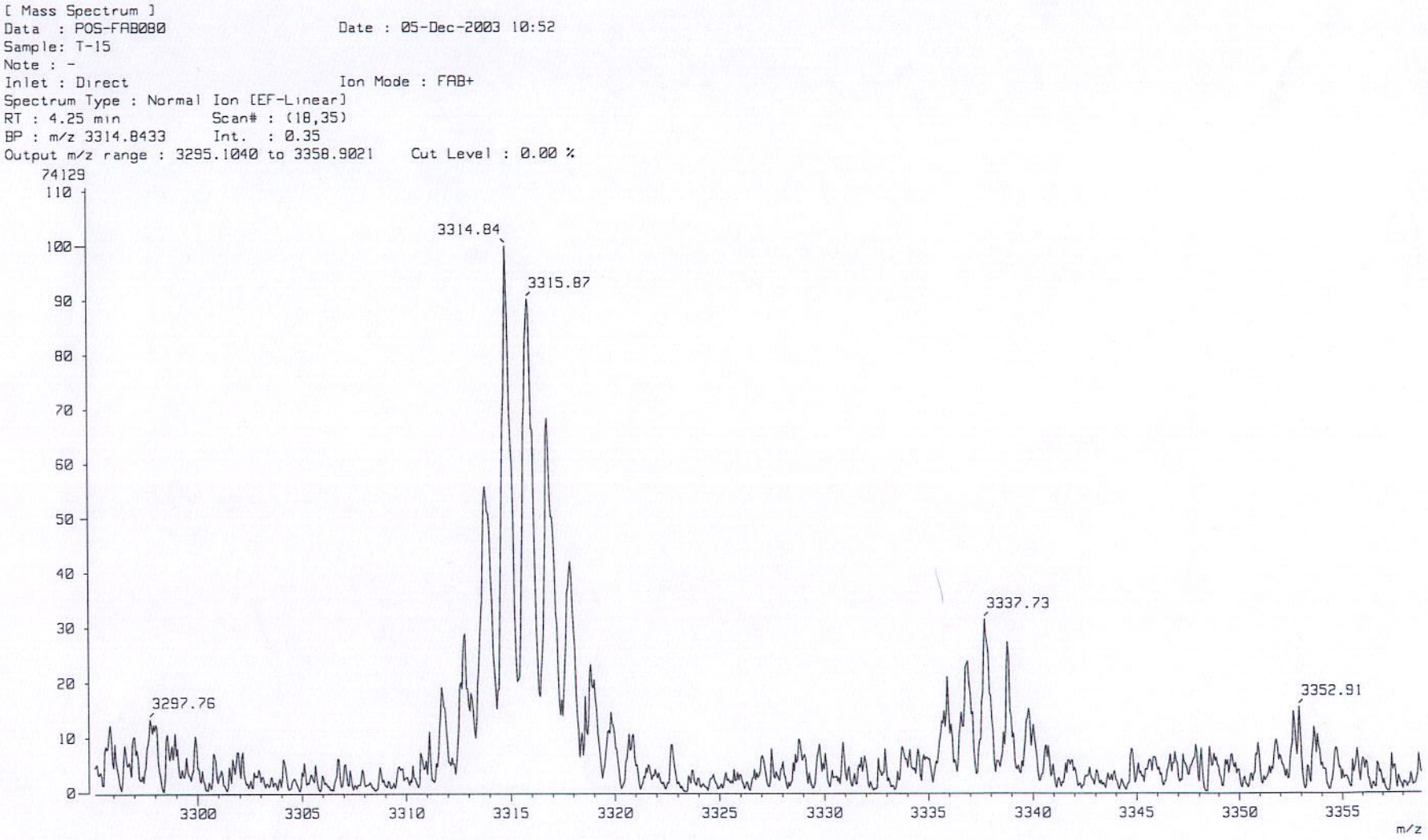


-8.8907 eV

-2.2829 eV

-1.5801 eV

FAB-MS (matrix : dithiothreitol / dithioerythritol = 3 / 1 , v / v) datum of γ -cyclodextrin-bicapped C_{60} (1)



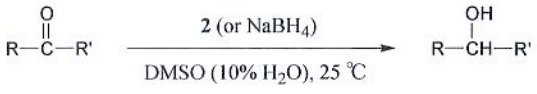
[Theoretical Ion Distribution]
Molecular Formula : C156 H161 O80
(m/z 3313.8530, MW 3315.9463, U.S. 76.5)
Base Peak : 3314.8564, Averaged MW : 3315.9503(a), 3315.9510(w)

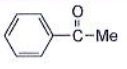
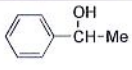
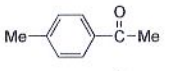
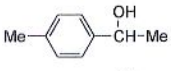
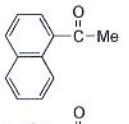
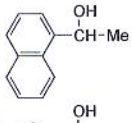
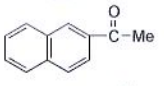
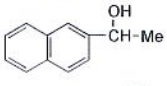
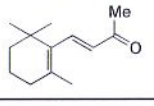
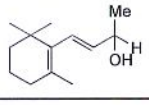
m/z	INT.	
3313.8530	55.8749	**********
3314.8564	100.0000	**********
3315.8596	97.9074	**********
3316.8626	68.4576	**********
3317.8656	38.0002	**********
3318.8685	17.7169	**********
3319.8713	7.1837	****
3320.8741	2.5935	**
3321.8768	0.8479	
3322.8795	0.2542	
3323.8822	0.0706	
3324.8849	0.0183	
3325.8876	0.0045	
3326.8902	0.0010	
3327.8928	0.0002	

[Elemental Composition]
Data : POS-FAB081 Date : 05-Dec-2003 11:42
Sample: T-15
Note : -
Inlet : Direct Ion Mode : FAB+
RT : 1.34 min Scan#: (2,16)+(43,65)+(92,105)
Elements : C 160/100, H 200/100, O 85/75
Mass Tolerance : 30mmu
Unsaturation (U.S.) : -0.5 - 100.0

Observed m/z	Int%	Err[ppm / mmu]	U.S.	Composition
3313.8718	65.9	+1.1 / +3.6	80.5	C 160 H 161 O 77
		-5.3 / -17.6	75.5	C 157 H 165 O 79
		+5.7 / +18.8	76.5	C 156 H 161 O 80
		-0.7 / -2.3	71.5	C 153 H 165 O 82
		-7.1 / -23.4	66.5	C 150 H 169 O 84
		+3.9 / +13.0	67.5	C 149 H 165 O 85

Table. Ketone reduction of γ-cyclodextrin-bicapped C_{60} dianion (**2**) or $NaBH_4$[a]



Entry	Substrate	Product[b]	Yield[c] (%)
1			100 (8) (32.3)[d]
2			100 (6) (28.4)[d]
3			100 (8) (52.1)[d]
4			100 (8) (42.5)[d]
5			100 (3) (33.8)[d]

a. Condition of parallel experiment: substrate (8-21 μ mol), reducing agent (1) **2** generated from **1** · $24H_2O$ (2.7 μ mol) and $NaBH_4$ (131.5 μ mol), and (2) $NaBH_4$ (131.5 μ mol) in the absence of **1** at 25 ℃, for 1 h.

b. Product is only the corresponding carbinol. No pinacole formation is observed.

c. Determined by GLC analysis: the value in parenthesis shows TOF (h^{-1}).

d. Control experiment with $NaBH_4$.