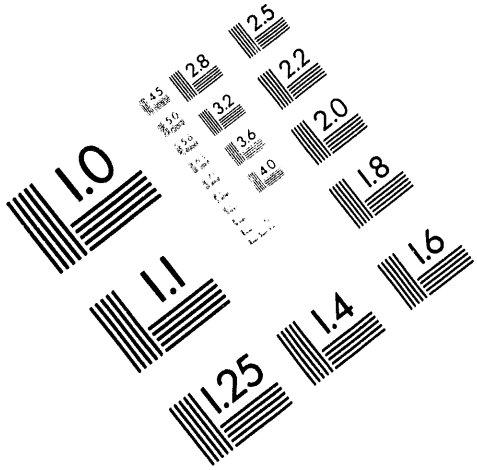

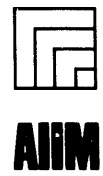

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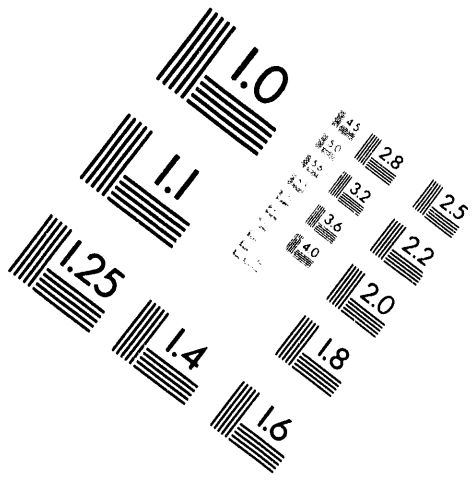

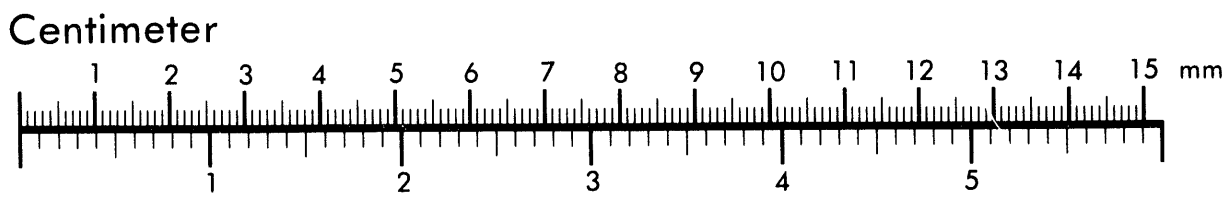

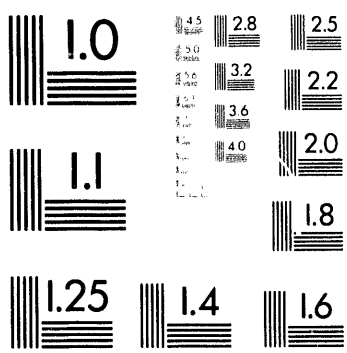

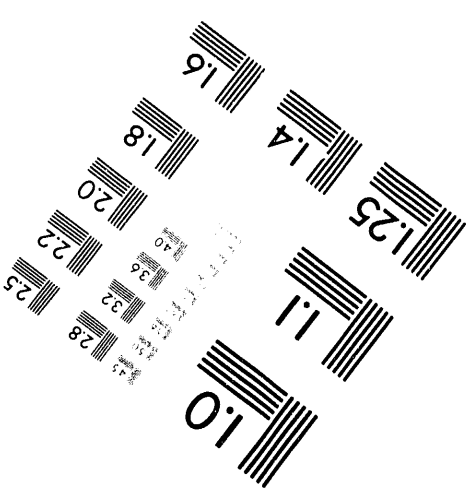

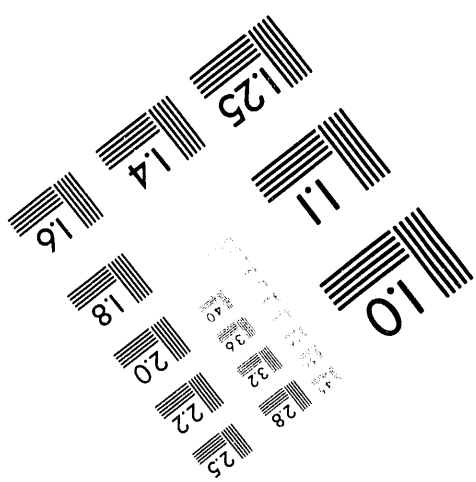

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THEORETICAL AND EXPERIMENTAL INVESTIGATIONS OF FULLERENE DERIVATIVES: $C_{60}H_2$, $C_{60}H_4$, $C_{70}H_2$, AND $C_{60}(CH_2)_2$

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ABSTRACT

Hydroboration of C_{70} in toluene yields a 2:1 mixture of 1,9-$C_{70}H_2$ and 7,8-$C_{70}H_2$. Equilibration of these two isomers in the presence of a Pt catalyst reveals a free energy difference of 1.4 ± 0.2 kcal/mol. Whereas semiempirical calculations have been found to predict the energy ordering of many fullerene derivatives incorrectly, ab initio Hartree-Fock (HF) calculations have been found to yield quantitative predictions of experiment. The HF/6-31G* level energy separation of 1,9-$C_{70}H_2$ and 7,8-$C_{70}H_2$ of 1.3 kcal/mol is in excellent agreement with experiment. Relative stabilities of isomers of bis(methano)fullerenes were found to parallel those of analogous $C_{60}H_4$ isomers. Density functional theory (DFT) methods have been tested and are equivalent in accuracy to HF methods if similar basis sets are used. $C_{60}H_2$ and $C_{60}H_4$ can be efficiently produced on larger ($\geq$ 50 mg) scales with diimide generated from potassium azodicarboxylate and acetic acid in *o*-dichlorobenzene.

INTRODUCTION

The addition chemistry of fullerenes continues to be rapidly explored.[1-11] Recent studies of derivatized fullerenes have demonstrated that such additions occur chemoselectively and generally under kinetic, not thermodynamic, control. Semiempirical predictions of the chemoselectivity of hydrogenation of C_{60} and C_{70} are *quantitatively* inaccurate and often *qualitatively* incorrect, but ab initio predictions of chemoselectivity are in quantitative agreement with experiment, albeit expensive. As part of continued investigations of addended C_{60} and C_{70}, which have provided fundamental insights about the addition chemistry of fullerenes, we report here (1) studies of 8 isomers of $C_{60}(CH_2)_2$ and (2) density functional theory (DFT) calculations on hydrogenated fullerenes for comparison with more expensive HF methods. Improvements in the synthesis of $C_{60}H_2$ have led to a facile, preparative scale synthesis of this compound.

SYNTHESIS

Addition of 2 eq of BH_3:THF to a toluene solution of C_{70} (0.5 mg/ml) at room temperature followed 1-2 hours later by quenching with a small volume (1-2% by volume) of water produced a solution of $C_{70}H_2$ isomers. The solution was dried over $MgSO_4$ and concentrated to 50% of its original volume. The products were isolated by HPLC (3:2 toluene:hexane, 10 mm $\times$ 25 cm Buckyclutcher I column,[12] 4.5 ml/min flow rate). The overall yield of $C_{70}H_2$ isomers was 20%. Conversion of pure 7,8-$C_{70}H_2$ to a mixture of 7,8- and 1,9-$C_{70}H_2$ (isomerization), and C_{70} (decomposition) was accomplished at room temperature in toluene solution over a platinum on silica catalyst. The composition of the mixture at various times was determined by HPLC with detection at 340 nm.

$C_{60}H_{2n}$ (n=1,2) were synthesized by dropwise addition of acetic acid (20 eq) to a suspension of potassium azodicarboxylate (10 eq) in a *o*-$C_6H_4Cl_2$ solution of C_{60} (20 mg/ml) under Ar at room temperature. The reaction mixture was shaken occasionally during a 10 minute period and filtered through a medium porosity fritted glass funnel. The solids were washed with a mixture of hexane and 1,2-$C_6H_4Cl_2$. The hexane was removed, and the products were separated via HPLC (3:1 hexane:1,2-$C_6H_4Cl_2$, 10 mm $\times$ 25 cm Buckyclutcher I column, 9 ml/min flow rate). The major components were C_{60} (45%), $C_{60}H_2$ (40%), and isomers of $C_{60}H_4$ (10%). Longer reaction times yielded significant amounts of products with longer HPLC retention times.

RESULTS AND DISCUSSION

Hydroboration of C_{70} followed by hydrolysis leads to a 2:1 mixture of 1,9- and 7,8-$C_{70}H_2$ (Fig. 1), which can be separated by HPLC.[11] Equilibration of these isomers occurs at room temperature in the presence of a platinum on silica catalyst. Under these conditions, both

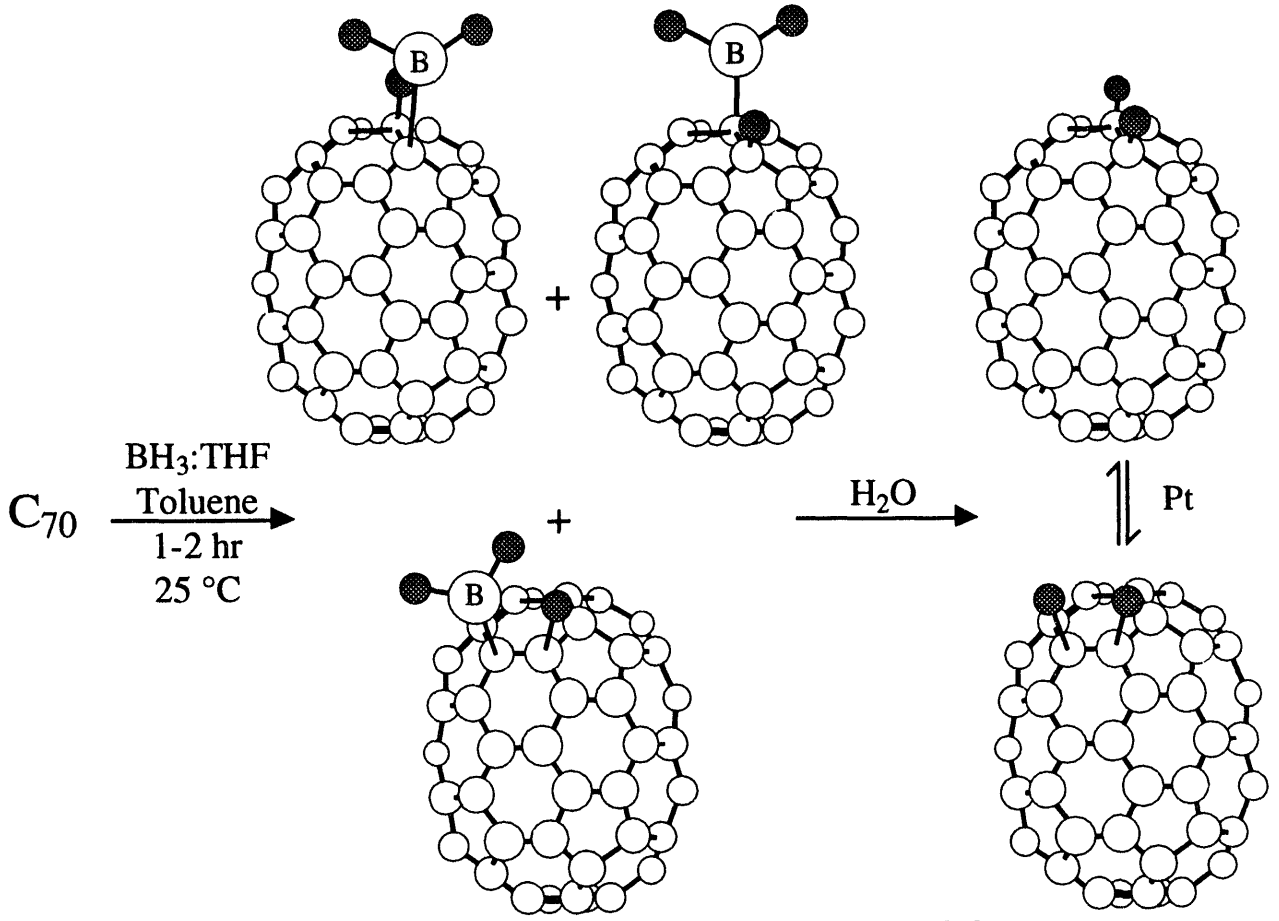


Figure 1. Synthesis and equilibration of 1,9- and 7,8-$C_{70}H_2$ (upper and lower right, respectively).

isomers also decompose to C_{70} in competing processes. The free energy difference between the two isomers of $C_{70}H_2$ was determined by kinetic analysis of the time evolution of the isomerization and decomposition of *pure* 7,8-$C_{70}H_2$ (Fig. 2) to 1,9-$C_{70}H_2$ and C_{70}.

If the kinetic scheme given by

$$C_{70} \xleftarrow{k_3} 7,8-C_{70}H_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 1,9-C_{70}H_2 \xrightarrow{k_2} C_{70}$$

accurately describes the dominant chemical reactions, it should be possible to obtain values for all four rate constants which lead to time-dependent concentration curves consistent with the experimental data. By letting A, B, and C represent the fractional composition of 7,8-$C_{70}H_2$, 1,9-$C_{70}H_2$, and C_{70}, respectively, simple kinetic analysis gives three rate equations:

$$\frac{dA}{dt} = -(k_1 + k_3)A + k_{-1}B$$

$$\frac{dB}{dt} = k_1 A - (k_{-1} + k_2)B$$

$$\frac{dC}{dt} = k_2 B + k_3 A .$$

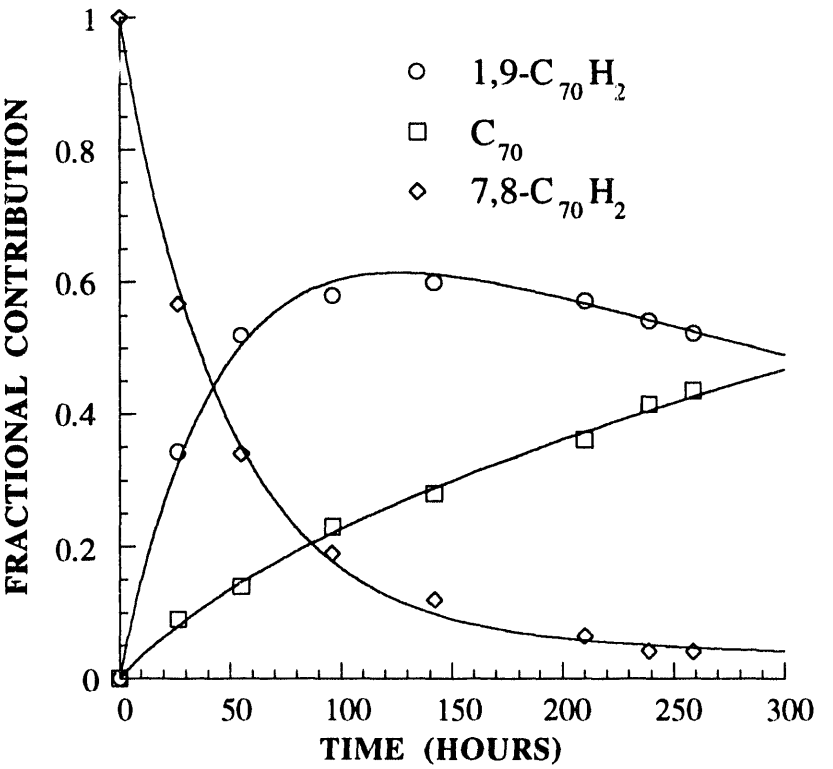


Figure 2. Time evolution of isomerization of 7,8-$C_{70}H_2$ over Pt/Si catalyst. The solid curves represent optimal numerical fits calculated on the basis of the proposed kinetic scheme

Numerical methods were used to generate theoretical concentration curves, and the parameters were optimized to arrive at both the optimum fit and error estimates. The results are: k_1 = 0.0165 ± 0.0015 h^{-1}, k_{-1} = 0.0015 ± 0.0004 h^{-1}, k_2 = 0.00166 ± 0.0002 h^{-1}, k_3 = 0.0035 ± 0.0005 h^{-1}. The high quality of the numerical fits obtained indicates that the proposed kinetic scheme is consistent with the experimental results. The equilibrium constant (k_1/k_{-1}) calculated from these parameters is 11 ± 2, which yields a ΔG_{295} = -1.4 ± 0.1 kcal/mol. Consideration of possible sources of systematic error, for example, from the approximation of equal molar absorptivities for all three species, leads to a larger error estimate in the ΔG_{295} than is required by the fit to the data. Therefore, a conservative estimate of the free energy difference between the 1,9 and 7,8 isomers is ΔG_{295} = 1.4 ± 0.2 kcal/mol, with the 1,9 isomer lying lower in energy. This value is in excellent agreement with the HF/6-31G* energy difference of 1.3 kcal/mol.

Geometry optimized HF/3-21G and HF/6-31G* calculations[13] were performed on the four lowest energy $C_{70}H_2$ isomers determined by MNDO-PM3 calculations. The two lowest energy isomers of $C_{70}H_2$ at all levels of theory are products of 1,2-addition to 6:6 ring fusions. The 7,8 isomer has the lowest calculated heat of formation in the semiempirical treatments. However, the 1,9-$C_{70}H_2$ isomer is favored by 1.3 kcal/mol over the 7,8 isomer at the most rigorous level of ab initio calculation (Table I).

The geometry optimizations of the $C_{70}H_2$ isomers at the HF/6-31G* level require approximately one CPU week on a Cray Y-MP. We therefore investigated the accuracy of more economical density functional methods using minimal basis sets for geometry optimization. The results are shown in Table I.

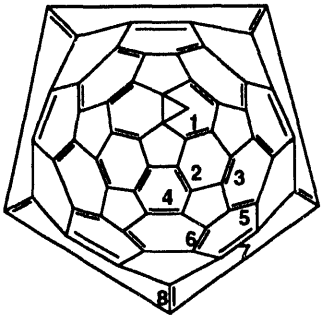
Table I. Relative energies of dihydrofullerenes at various levels of theory (kcal/mol).

		MNDO-PM3[8]	HF-3/21G[8]	HF/6-31G*[8]	**BLYP/STO-3G**	Expt.
$C_{60}H_2$	1,2	0.0	0.08	0.08	**0.0**	
	1,4	3.9	7.8	7.6	**7.9**	
	1,16	15.5	23.1	20.9		
	1,6	18.4	26.4	24.0		
$C_{70}H_2$	1,9	0.0	0.0	0.0	**0.0**	
	7,8	-1.1	0.2	1.3	**2.8**	1.4±0.2[11]
	21,42	0.3	2.1	4.5		
	1,7	1.4	5.8	6.4		

The Becke-Lee-Yang-Parr combination of functionals with a minimal STO-3G basis set yields qualitatively and in some cases quantitatively correct results in less time than is required for HF/3-21G calculations. The energy separation of 1,2-$C_{60}H_2$ and 1,4-$C_{60}H_2$ calculated at BLYP/STO-3G is 7.9 kcal/mol vs. 7.6 kcal/mol at HF/6-31G*. However, the energy separations of 1,9-$C_{70}H_2$ and 7,8-$C_{70}H_2$ are 2.88 kcal/mol at BLYP/STO-3G and 1.3 kcal/mol at HF/6-31G*, a substantial difference. The BLYP/STO-3G geometries also differ substantially from those at the higher levels of theory (Table II), and are therefore not reliable. However, the time and cost savings of DFT versus very high level HF calculations are substantial, and investigations with DFT calculations continue.

Table II. Comparison of calculated bond lengths (Å).

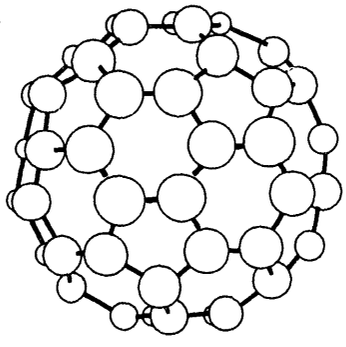
		MNDO-PM3[8]	HF/3-21G[8]	HF/6-31G*[8]	**BLYP/STO-3G**	Expt.
C_{60}	1,2	1.362	1.367	1.373	**1.429**	1.401[15]
	1,9	1.457	1.453	1.449	**1.490**	1.458
C_{70}	1,2	1.457	1.452	1.446	**1.489**	1.46[16];1.464[17]
	1,9	1.386	1.370	1.375	**1.430**	1.38; 1.37
	6,7	1.453	1.447	1.442	**1.485**	1.45; 1.47
	7,8	1.374	1.356	1.363	**1.422**	1.37; 1.37
	7,22	1.463	1.458	1.453	**1.485**	1.43; 1.46
	21,22	1.426	1.414	1.413	**1.468**	1.44; 1.47
	21,40	1.412	1.403	1.406	**1.455**	1.42; 1.39
	23,24	1.463	1.475	1.472	**1.504**	1.46; 1.41
$C_{60}H_2$	sp^3-sp^3	1.562	1.586	1.582	**1.625**	
$C_{70}H_2$	1,9 sp^3-sp^3	1.565	1.588	1.583	**1.625**	
	7,8 sp^3-sp^3	1.546	1.567	1.565	**1.610**	



Multiple addition of carbenes to yield bis(methano)fullerenes have been proposed as a method of synthesizing "pearl chain necklace" polymers.[17-25] The results of a computations of the relative stability of 8 isomers of $C_{60}(CH_2)_2$ are listed in Table III. The relative isomer energies indicate that in the absence of steric effects there will be little thermodynamic preference for the site of second carbene addition. Furthermore, the results suggest that the synthesis of polymers with regular structures ...-C_{60}-alkyl-C_{60}-alkyl-... in which the alkyl chains are diametrically opposed will be difficult by a biscarbene approach.

Table III. Calculated energies of dimethanofullerenes $C_{60}(CH_2)_2$.					
		MNDO-PM3 (kcal/mol)	Relative (kcal/mol)	HF/3-21G (a.u.)	Relative (kcal/mol)
$C_{60}(CH_2)$		808.10			
$:CH_2$		113.22			
$C_{60}(CH_2)_2$	1	803.19	0.00	-2336.652136	0.00
	2	806.83	3.64	-2336.642894	5.80
	3	806.41	3.22	-2336.644256	4.94
	4	804.35	1.16	-2336.649117	1.89
	5	804.61	1.42	-2336.647919	2.65
	6	804.60	1.41	-2336.648795	2.09
	7	804.66	1.47	-2336.648510	2.28
	8	804.63	1.44	-2336.648225	2.45

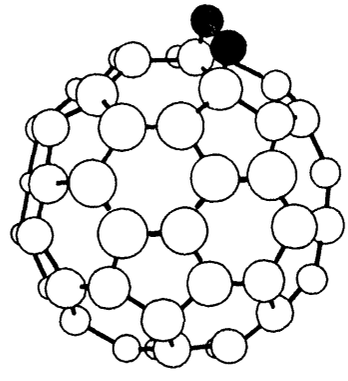
Larger quantities of $C_{60}H_2$ and $C_{60}H_4$ are more easily prepared with diimide[3] than our originally reported, borane method. Both the conversion and yield of the reduction of C_{60} to $C_{60}H_2$ and $C_{60}H_4$ are improved by changing from borane to diimide[3] and from toluene to *o*-dichlorobenzene.[26,27]



20 mg/ml o-$C_6H_4Cl_2$

+ $KO_2CN{=}NCO_2K$
10 eq

20 eq AcOH
10 min @ r.t.
filter
inject on HPLC



55% conversion
73% yield (consumed C_{60})

The quantifiable nature of potassium azodicarboxylate and acetic acid[28] allows exact control over the stoichiometry of the reaction. Contact time with the reducing agent is crucial to success, with short reaction times producing the best yields of simple hydrofullerenes. The optimized yield of $C_{60}H_2$ is doubled, and the speed of the purification is increased two- to threefold because of the increased solubility of the products in 3:1 hexane:*o*-dichlorobenzene vs. 1:1 hexane:toluene. Up to 50 mg of $C_{60}H_2$ may be produced and isolated per day on a 10 mm × 250 mm Buckyclutcher I column.

Acknowledgements

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