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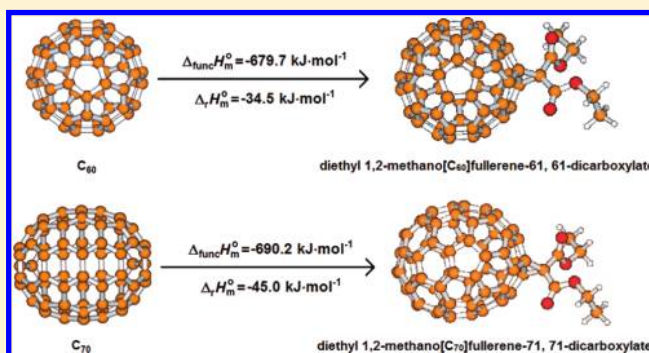
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Enthalpies of Formation and of Functionalization Reactions for Bingel-Type Monoadducts of C<sub>60</sub> and C<sub>70</sub> Using MicrocalorimetryMelchor Martínez-Herrera,<sup>†</sup> Patricia Amador,<sup>‡</sup> and Aarón Rojas<sup>\*,†</sup><sup>†</sup>Departamento de Química del Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional, Avenida Instituto Politécnico Nacional 2508, México D.F., C.P. 07360, Mexico<sup>‡</sup>Facultad de Ciencias Químicas, Benemérita Universidad Autónoma de Puebla, Avenida San Claudio y 14 Sur, Puebla, Puebla, C.P. 72570, Mexico

## S Supporting Information

**ABSTRACT:** The molar standard enthalpies of combustion and formation of the Bingel-type monoadducts diethyl 1,2-methano-[C<sub>60</sub>]fullerene-61, 61-dicarboxylate, C<sub>61</sub>(COOEt)<sub>2</sub>, and diethyl 1,2-methano[C<sub>70</sub>]fullerene-71, 71-dicarboxylate, C<sub>71</sub>(COOEt)<sub>2</sub>, have been determined as 1613.4 ± 37.6 and 1847.2 ± 37.0 kJ·mol<sup>-1</sup>, respectively. These values were obtained based on their energies of combustion, as measured by microcombustion calorimetry. With these values and the molar standard enthalpies of formation for C<sub>60</sub> and C<sub>70</sub>, the enthalpic contributions for the functionalization of both fullerenes were calculated as  $\Delta_{\text{func}}H_m^\circ[\text{C}_{60}(\text{cr}) \rightarrow \text{C}_{61}(\text{COOEt})_2(\text{cr})] = -679.7 \text{ kJ}\cdot\text{mol}^{-1}$  and  $\Delta_{\text{func}}H_m^\circ[\text{C}_{70}(\text{cr}) \rightarrow \text{C}_{71}(\text{COOEt})_2(\text{cr})] = -690.2 \text{ kJ}\cdot\text{mol}^{-1}$ . The standard enthalpies associated with the functionalization reactions were found to be  $\Delta_f H_m^\circ[\text{C}_{60}(\text{cr}) \rightarrow \text{C}_{61}(\text{COOEt})_2(\text{cr})] = -34.5 \text{ kJ}\cdot\text{mol}^{-1}$  and  $\Delta_f H_m^\circ[\text{C}_{70}(\text{cr}) \rightarrow \text{C}_{71}(\text{COOEt})_2(\text{cr})] = -45.0 \text{ kJ}\cdot\text{mol}^{-1}$ . These results show that the insertion of the bis(ethoxycarbonyl)methane group on the C<sub>70</sub> sphere to obtain C<sub>71</sub>(COOEt)<sub>2</sub> produced an enthalpic change that was more exothermic than that produced when the same group was inserted on C<sub>60</sub>. Thus, the formation of C<sub>71</sub>(COOEt)<sub>2</sub>(cr) was favored over C<sub>61</sub>(COOEt)<sub>2</sub>(cr) by 10.5 kJ·mol<sup>-1</sup>. Theoretical enthalpies and Gibbs energies of the functionalization reactions, computed using density functional theory (DFT) at the B3LYP/3-21G\*, B3LYP/6-31G, and B3LYP/6-31G\* levels of theory, agreed with the experimental results presented here.



## 1. INTRODUCTION

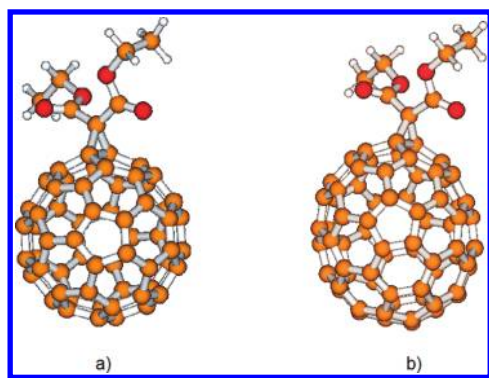
Since fullerenes became available in macroscopic quantities in 1990,<sup>1</sup> these new carbon structures have gained a primary role on the scientific scene. Fullerenes have generated exhaustive academic and industrial interest that has led to the discovery of many of their interesting physical and chemical properties.<sup>2</sup> Upon their discovery, it was immediately clear that this new molecular material had enormous potential toward multiple disciplines. However, the low solubility of fullerenes in organic solvents has presented a serious obstacle in the search for practical applications. This major problem has encouraged chemists to design and synthesize functionalized fullerene derivatives.<sup>3</sup> The main advantage of functionalized fullerenes is the substantial increase in their solubility that can be generated by the insertion of polar molecular groups. The special characteristics of the addend groups, coupled with the unique structural, physicochemical, and electronic properties of fullerenes, have aided the development of new fullerene derivatives, which are interesting from both fundamental and potential technological viewpoints, rendering them suitable candidates for many technological applications that range from medicine to electronics.<sup>4</sup>

Fullerenes provide fascinating carbon skeletons for endo- and exohedral chemical modifications. These molecules can be functionalized in three dimensions owing to the spherical structure of their regularly arranged, unsaturated carbon centers.<sup>3a</sup> The covalent functionalization of fullerenes has been vigorously developed, and this is particularly evident for the most abundant carbon sphere, known as buckminsterfullerene (C<sub>60</sub>).<sup>3a</sup> A rich variety of methods for the preparation of covalent monoadducts are known, in which a fullerene reacts as a strained, electron-deficient polyalkene with rather localized bonds.<sup>5</sup> Among the established functionalization methods, the cyclopropanation of fullerenes with malonates has attracted particular attention because of the interesting electronic characteristics of the resulting structures, as well as the ease with which the functional group attached indirectly to a cluster can be varied.<sup>6</sup> Examples of this are the methanofullerenes that bear carboxy groups. These have been prepared by the direct reaction of C<sub>60</sub> or C<sub>70</sub> with malonate esters or bromomaltonates in the presence

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**Figure 1.** Molecular structure of the Bingel-type monoadducts of  $C_{60}$  and  $C_{70}$ : (a) diethyl 1,2-methano[ $C_{60}$ ]fullerene-61, 61-dicarboxylate ( $C_{61}(\text{COOEt})_2$ ); (b) diethyl 1,2-methano[ $C_{70}$ ]fullerene-71, 71-dicarboxylate ( $C_{71}(\text{COOEt})_2$ ).

of  $\text{CBr}_4$  and different bases, such as 1,8-diazabicyclo[5,4,0]undec-7-ene, NaH, or sodium acetate, to afford cyclopropane derivatives, such as the monoadduct diethyl 1,2-methano[ $C_{60}$ ]fullerene-61, 61-dicarboxylate ( $C_{61}(\text{COOEt})_2$ , Figure 1a) and diethyl 1,2-methano[ $C_{70}$ ]fullerene-71, 71-dicarboxylate ( $C_{71}(\text{COOEt})_2$ , Figure 1b). These Bingel-type methanofullerenes have been utilized as building blocks for the synthesis of highly water-soluble dendrimers, as well as for highly symmetrical and stereochemically defined oligoadducts. These compounds have potentially useful properties for biological chemistry and materials science.<sup>7</sup>

The synthesis, reactivity, and potential applications of functionalized fullerenes have been intensively studied. However, research into the thermodynamic properties of these functionalized clusters remains undeveloped. Many properties of these fullerene derivatives are new or unusual, and thermochemical data are useful to gain an understanding between the structure and energetics of this particular set of compounds. Two thermochemical studies into the enthalpy of formation and the heat of functionalization for the methanofullerene derivatives has been reported at this time in this journal.<sup>8</sup> Giving continuity to that research, in the current work calculating the enthalpies of formation for  $C_{61}(\text{COOEt})_2(\text{cr})$  and  $C_{71}(\text{COOEt})_2(\text{cr})$  would demonstrate if the insertion of the same functional group into different fullerenes produces the same enthalpic contribution or if the dissimilar molecular structures of the fullerenes causes an additional enthalpic effect.

In this work, we carried out the synthesis of the monoadducts  $C_{61}(\text{COOEt})_2(\text{cr})$  and  $C_{71}(\text{COOEt})_2(\text{cr})$  by the procedure published by Camps and Hirsch,<sup>6c</sup> followed by the measurement of their molar standard energies of combustion and derivation of their molar standard enthalpies of combustion and formation using a microcombustion bomb set. This set was associated with a Calvet-type heat-flux microcalorimeter and around 2 mg of sample per combustion experiment. This methodology has already been successfully applied to measure the energies of combustion and derive the enthalpies of formation for coronene, the pure fullerenes ( $C_{60}$ ,  $C_{70}$ ,  $C_{76}$ ,  $C_{78}$ , and  $C_{84}$ ), and a functionalized fullerene.<sup>8,9</sup> The molar standard enthalpies of formation for the Bingel-type monoadducts  $C_{61}(\text{COOEt})_2$  and  $C_{71}(\text{COOEt})_2$ , as well as the enthalpies of formation for  $C_{60}$  and  $C_{70}$ ,<sup>9b</sup> were utilized to calculate the enthalpies of functionalization for the insertion of a bis-(ethoxycarbonyl)methano group into a double bond of either a

$C_{60}$  or a  $C_{70}$  sphere. The enthalpies of the functionalization reactions have been compared with those estimated by density functional theory (DFT) at the B3LYP/3-21G\*, B3LYP/6-31G, and B3LYP/6-31G\* levels of theory.

## 2. EXPERIMENTAL SECTION

**2.1. Synthesis and Characterization.** The Bingel-type monoadducts  $C_{61}(\text{COOEt})_2$  and  $C_{71}(\text{COOEt})_2$  were synthesized by cyclopropanation of  $C_{60}$  and  $C_{70}$  starting from diethyl malonate,  $\text{CBr}_4$ , and in the presence of the base 1,8-diazabicyclo[5,4,0]undec-7-ene.<sup>6c</sup> Chromatographic separation of the reaction mixture ( $\text{SiO}_2$ ) with *n*-hexane/toluene (65:35) gave in both cases a first fraction consisting of residual amount of  $C_{60}$  or  $C_{70}$ . Subsequently, pure toluene was used to yield a second fraction that consisted of the monoadduct contaminated with traces of  $C_{60}$  or  $C_{70}$ . Finally, a fraction containing an isomeric mixture of the corresponding bisadducts was obtained. Chromatography was also carried out for the second fraction using silica gel with *n*-hexane/toluene (65:35) and pure toluene to remove the traces of  $C_{60}$  or  $C_{70}$  and to obtain pure monoadduct. The purity of both samples was verified by high-pressure liquid chromatography (HPLC) using a Waters 600 chromatograph equipped with a diode array detector and a Develosil C30-UG-5 analytical column with toluene/acetonitrile (38:62) as the eluent. The samples of  $C_{61}(\text{COOEt})_2$  and  $C_{71}(\text{COOEt})_2$  were characterized by  $^1\text{H}$  nuclear magnetic resonance (NMR), ultraviolet–visible (UV–vis) and infrared (IR) spectroscopies, as well as electrospray ionization mass spectrometry (ESI-MS). The data obtained are as follows.  $C_{61}(\text{COOEt})_2$ :  $^1\text{H}$  NMR (400 MHz,  $\text{CS}_2\text{—CDCl}_3$ ),  $\delta$  4.54 (q,  $J = 7$  Hz, 4H), 1.52 (t,  $J = 7$  Hz, 6H); UV–vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}/\text{nm}$  258, 324, 426; IR(KBr)/ $\text{cm}^{-1}$  1743, 1460, 1427, 1385, 1364, 1292, 1265, 1233, 1177, 1094, 1059, 1020, 856, 735, 704, 579, 551, 525; MS [ESI-time-of-flight (TOF)] ( $m/z$ ) 878.059 ( $M^-$ ). For  $C_{71}(\text{COOEt})_2$ , the  $^1\text{H}$  NMR spectrum showed only one triplet for the methyl protons and a multiplet for the diastereotopic methylene protons of the two malonate ethoxy-ester units, indicating that the monoadduct existed as a single isomer, “ $\alpha$ -type” (Figure 1b).<sup>10</sup> On the other hand, the minor isomer “ $\beta$ -type” was not detected, which is in agreement with the report by Bingel and Schiffer.<sup>6b</sup> Results obtained for this compound are as follows:  $^1\text{H}$  NMR (400 MHz,  $\text{CS}_2\text{—CDCl}_3$ ),  $\delta$  4.50 (m, 4H), 1.50 (t,  $J = 7$  Hz, 6H); UV–vis ( $\text{CHCl}_3$ )  $\lambda_{\text{max}}/\text{nm}$  241, 324, 352, 370, 402, 461, 538, 608, 659; IR(KBr)/ $\text{cm}^{-1}$  1746, 1510, 1499, 1428, 1228, 1093, 1018, 796, 670, 578, 535, 459; MS (ESI-TOF) ( $m/z$ ) 999.066 ( $M^+$ ). Data from all spectra are in good agreement with those reported by Bingel and co-workers and Peng et al. for these fullerene derivatives.<sup>6a,b,11</sup>

**2.2. Microcombustion Calorimetry.** The massic energies of combustion,  $\Delta_c u^\circ(\text{cr})$ , for the monoadducts of  $C_{60}$  and  $C_{70}$  were measured using a microbomb set and a Setaram C80 Calvet-type heat-flux microcalorimeter operated isothermally at 303.15 K.<sup>8,9</sup> The microcalorimeter sensors were two flux meters with power detection limits of 2  $\mu\text{W}$  and calorimetric resolutions of 0.1  $\mu\text{W}$ . The sensors were assembled inside a calorimetric block with a temperature control of at least  $\pm 0.01$  K. The design and adaptation of the microbomb set to the microcalorimeter have been previously described in the literature.<sup>12</sup>

Before measuring the energies of combustion of both monoadducts, the measurement microbomb setup was calibrated using combustion experiments with a standard reference sample of benzoic acid. The electric firing required for ignition of the

sample of  $C_{61}(\text{COOEt})_2(\text{cr})$  was determined prior to or after the combustion experiment using the C80 microcalorimeter and the same platinum thread. For  $C_{71}(\text{COOEt})_2(\text{cr})$ , the electric firing energy required for ignition was independently determined to be  $1.275 \pm 0.020$  J from the average of 12 experiments. The resulting ignition energy was taken into account in the calculation of the calorimetric constant of the microbomb, as well as the calculation of the energies of combustion for each monoadduct.

Each sample of  $C_{61}(\text{COOEt})_2(\text{cr})$  and  $C_{71}(\text{COOEt})_2(\text{cr})$  involved in a combustion experiment was pelletized using a Parr pellet press and a 2.38 mm stainless steel punch and die set. Combustion experiments with approximately 2 mg pellets were carried out in an oxygen atmosphere at 3.04 MPa and a temperature of 303.15 K. To promote total oxidation of the samples, solid Vaseline was used to aid combustion. The standard massic energy of combustion of the Vaseline was previously measured (see the Supporting Information) using a macro static-bomb combustion calorimeter. Unburned traces of reactants were not detected by visual inspection of the microbomb crucible following combustion. Additional methodologies have been described in detail elsewhere, including the flushing technique that has been used to ensure the absence of nitrogen inside of the microbomb, complete filling with oxygen at 3.04 MPa, and the use of adequate periods for thermal stabilization and data acquisition.<sup>9b,12</sup>

The mass of each monoadduct pellet and all the other substances involved in each combustion experiment was measured using a Mettler-Toledo UMX2 microbalance, which was sensitive to 0.1  $\mu\text{g}$  (precision:  $\pm 0.1 \mu\text{g}$ ). Corrections for apparent mass to mass and corrections to the standard state were performed with computer software written in the laboratory, with the latter being based on the Washburn corrections.<sup>13</sup> The required massic heat capacities, energies of combustion of the auxiliary materials, and  $(\partial U/\partial P)_T$  data for  $C_{61}(\text{COOEt})_2(\text{cr})$  and  $C_{71}(\text{COOEt})_2(\text{cr})$ , the cotton, and the Vaseline can be found in the Supporting Information.

### 3. COMPUTATIONAL DETAILS

The theoretical enthalpies of formation for  $C_{61}(\text{COOEt})_2(\text{g})$  and  $C_{71}(\text{COOEt})_2(\text{g})$  were estimated from DFT, using Bingel reaction as a model and involving  $C_{60}$ , diethyl malonate, bromide, and sodium hydride. The geometry of all compounds involved was fully optimized using DFT, according to Becke's three-parameter gradient-corrected exchange functional and the Lee–Yang–Parr (LYP) gradient-corrected correlation functional (B3LYP).<sup>14</sup> The 3-21G\*, 6-31G, and 6-31G\* basis sets were utilized without symmetry constraints, except for  $C_{60}$  and  $C_{70}$ . Vibration frequencies were calculated using the same basis set for the optimum B3LYP/3-21G\* and B3LYP/6-31G molecular geometries obtained to guarantee that the optimized structures were minima on the potential energy surfaces and to obtain thermal corrections to enthalpy at a temperature of 298 K. Vibration frequencies were not computed at the optimum B3LYP/6-31G\* level because of computational limitations. Nevertheless, the resulting enthalpies of formation obtained from the enthalpies of reaction at the B3LYP/3-21G\* and B3LYP/6-31G levels of theory without the thermal correction at  $T = 298$  K did not change significantly. This finding demonstrates that such an approximation makes it possible to employ energies at  $T = 0$  K rather than the standard enthalpies. This computational procedure eliminates the need for the

**Table 1. Mass and Energy Data for a Representative Combustion Experiment with the Monoadducts  $C_{61}(\text{COOEt})_2$  and  $C_{71}(\text{COOEt})_2$  at 303.15 K ( $p^\circ = 0.1$  MPa)**

	$C_{61}(\text{COOEt})_2(\text{cr})$	$C_{71}(\text{COOEt})_2(\text{cr})$
$m(\text{sample})/\text{mg}^a$	1.5854	1.3767
$m(\text{Vaseline})/\text{mg}^b$	0.8315	0.6567
$m(\text{cotton})/\text{mg}^c$	0.3842	0.2750
$A/\text{J}^d$	−98.853	−81.809
$\Delta U_{\text{IBP}}/\text{J}^e$	−99.814	−82.646
$\Delta U_{\text{ign}}/\text{J}^f$	1.740	1.275
$\Delta U_w/\text{J}^g$	0.052	0.044
$m\Delta_c u^\circ(\text{Vaseline})/\text{J}$	−38.585	−30.473
$m\Delta_c u^\circ(\text{cotton})/\text{J}$	−6.381	−4.568
$m\Delta_c u^\circ(\text{sample})/\text{J}$	−53.057	−46.287
$\Delta_c u^\circ(\text{sample})/\text{J} \cdot \text{g}^{-1}$	−33465.9	−33621.6

<sup>a</sup> Mass of the monoadduct of  $C_{60}$  or  $C_{70}$ . <sup>b</sup> Mass of Vaseline used as a combustion aid. <sup>c</sup> Mass of cotton used as a fuse. <sup>d</sup> Area under the calorimetric curve. <sup>e</sup> Internal energy change for the isothermal bomb process. <sup>f</sup> Electric energy for the ignition. <sup>g</sup> Correction to the standard state.

**Table 2. Massic Standard Energies at  $T = 303.15$  K ( $p^\circ = 0.1$  MPa) Resulting from Five Combustion Experiments with the Monoadducts of  $C_{60}$  and  $C_{70}$ <sup>a</sup>**

experiment	$C_{61}(\text{COOEt})_2$	$C_{71}(\text{COOEt})_2$
1	−33465.9	−33621.6
2	−33444.1	−33591.8
3	−33505.3	−33607.7
4	−33439.9	−33604.9
5	−33452.6	−33631.3
$\langle \Delta_c u^\circ / \text{J} \cdot \text{g}^{-1} \rangle$	−33461.5 $\pm$ 11.8	−33611.5 $\pm$ 6.9

<sup>a</sup> The uncertainty associated with the average value is the standard deviation of the mean.

prohibitively expensive computation of zero-point energies and thermal corrections at the B3LYP/6-31G\* level. All calculations were carried out with the Gaussian 98 software.<sup>15</sup>

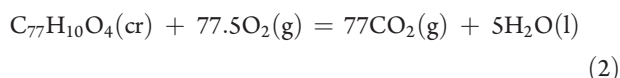
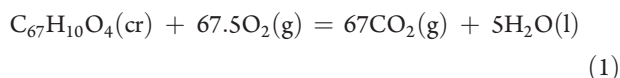
### 4. RESULTS AND DISCUSSION

The calorimetric constant,  $k_m$ , of the microbomb utilized in the measurements of the energy of combustion of  $C_{61}(\text{COOEt})_2(\text{cr})$  was determined to be  $1.009724 \pm 0.00026$  by nine combustions of standard NIST 39j benzoic acid. In order to keep a high accuracy in the results of energy of combustion, prior to the measurements on the  $C_{71}(\text{COOEt})_2(\text{cr})$ ,  $k_m$  was re-determined as  $1.010232 \pm 0.00027$  through 10 combustions of the standard benzoic acid. By utilizing such calorimetric constants, the internal energy change for the isothermal bomb process was calculated as  $\Delta U_{\text{IBP}} = Ak_m$ , where  $A$  is the area of the combustion curve of each fullerene derivative. Detailed mass and energy quantities of a representative combustion experiment on  $C_{61}(\text{COOEt})_2(\text{cr})$  and  $C_{71}(\text{COOEt})_2(\text{cr})$  at 303.15 K are shown in Table 1.

From five experimental results for each monoadduct shown in Table 2, the average massic standard energies of combustion,  $\langle \Delta_c u^\circ \rangle$ , were found to be  $−33461.5 \pm 11.8$  and  $−33611.5 \pm$



$6.9 \text{ J} \cdot \text{g}^{-1}$  for  $\text{C}_{61}(\text{COOEt})_2(\text{cr})$  and  $\text{C}_{71}(\text{COOEt})_2(\text{cr})$ , respectively, at 303.15 K. These standard energies are related to the ideal combustion reactions:



where the reactants and products are in thermodynamic standard states. The molar standard energies of combustion,  $\Delta_c U_m^\circ(\text{cr})$ , were computed from the average massic energy of combustion.

**Table 3. Summary of the Thermodynamic Properties (in  $\text{kJ} \cdot \text{mol}^{-1}$ ) That Were Measured and Derived for the Monoadducts of  $\text{C}_{60}$  and  $\text{C}_{70}$ <sup>a</sup>**

	$\text{C}_{61}(\text{COOEt})_2$	$\text{C}_{71}(\text{COOEt})_2$
$\Delta_c U_m^\circ(\text{cr}), T = 303.15 \text{ K}$	$-29405.8 \pm 32.8$	$-33574.5 \pm 31.1$
$\Delta_c H_m^\circ(\text{cr}), T = 303.15 \text{ K}$	$-29407.1 \pm 32.8$	$-33575.8 \pm 31.1$
$\Delta_c H_m^\circ(\text{cr}), T = 298.15 \text{ K}$	$-29407.8 \pm 32.8$	$-33576.6 \pm 31.1$
$\Delta_f H_m^\circ(\text{cr}), T = 298.15 \text{ K}$	$1613.4 \pm 37.2$	$1847.2 \pm 37.0$

<sup>a</sup>The quoted dispersions are twice the overall uncertainty (ref 17).

From eqs 1 and 2 and the average massic energy of combustion, the corresponding molar standard enthalpies of combustion,  $\Delta_c H_m^\circ$ , at 303.15 K, were calculated as follows:

$$\Delta_c H_m^\circ[\text{C}_{61}(\text{COOEt})_2(\text{cr}), 303.15 \text{ K}] = \Delta_c U_m^\circ[\text{C}_{61}(\text{COOEt})_2(\text{cr}), 303.15 \text{ K}] - 0.5RT \quad (3)$$

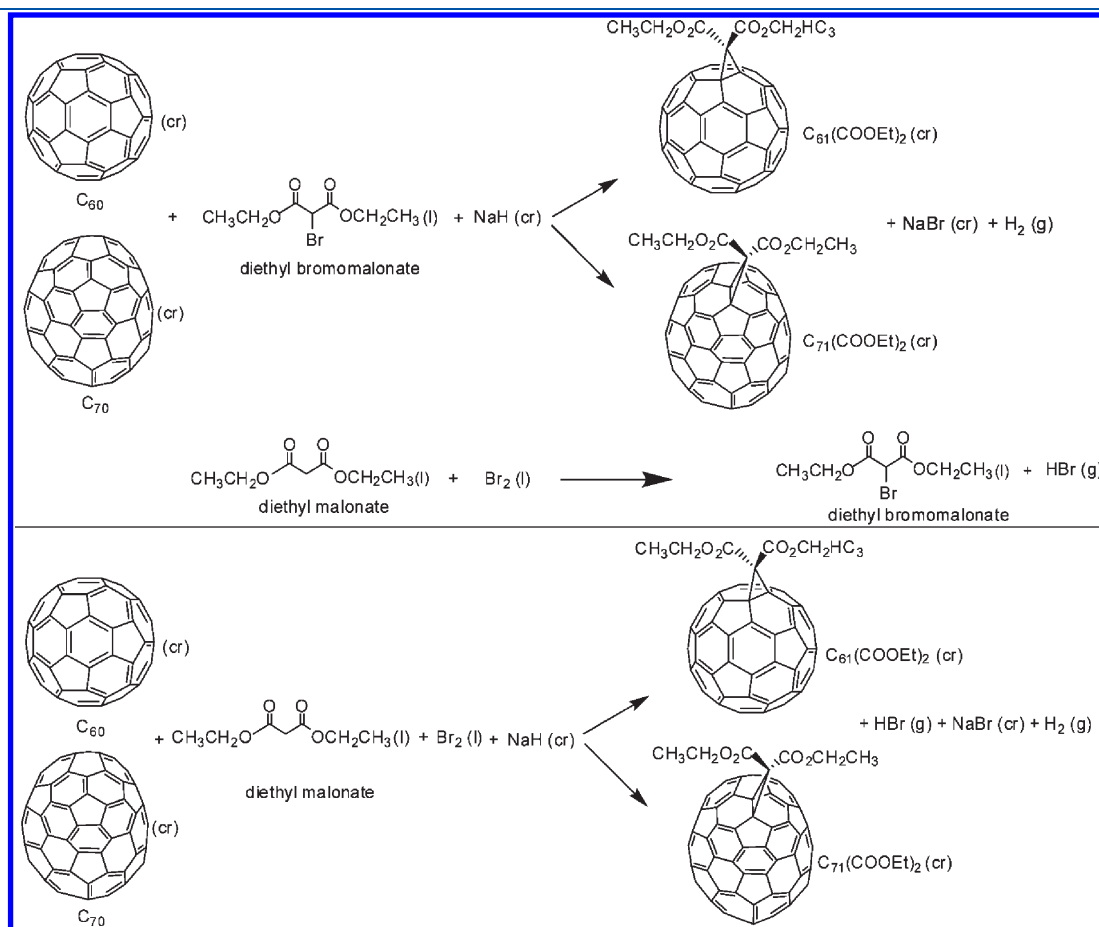
$$\Delta_c H_m^\circ[\text{C}_{71}(\text{COOEt})_2(\text{cr}), 303.15 \text{ K}] = \Delta_c U_m^\circ[\text{C}_{71}(\text{COOEt})_2(\text{cr}), 303.15 \text{ K}] - 0.5RT \quad (4)$$

In eqs 3 and 4, the factor  $RT$  is multiplied by the differences in the stoichiometric coefficients for the gas phase of products and reactants in the combustion reactions 1 and 2.

The molar standard enthalpies of combustion at 298.15 K were derived from the data at 303.15 K using the following equation:

$$\Delta_c H_m^\circ(\text{cr}, 298.15 \text{ K}) = \Delta_c H_m^\circ(\text{cr}, 303.15 \text{ K}) - \int_{298.15\text{K}}^{303.15\text{K}} \Delta C_{p,m} dT \quad (5)$$

where the value of  $\Delta C_{p,m}$  for the combustion process was calculated from molar heat capacity data at constant pressure of the substances involved in the combustion reaction. For each solid monoadduct, the heat capacity datum was experimentally determined via differential scanning calorimetry (see the Supporting Information), whereas for the gases in the combustion reaction, the taken molar heat capacities were  $29.387 \pm 0.003$ ,



**Figure 2.** Hess's Law involving Bingel's reaction for calculating the enthalpy of the functionalization reactions of  $\text{C}_{60}$  and  $\text{C}_{70}$  to give the monoadducts  $\text{C}_{61}(\text{COOEt})_2$  and  $\text{C}_{71}(\text{COOEt})_2$ , respectively.

$37.220 \pm 0.002$ , and  $75.349 \pm 0.080 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  for  $\text{O}_2(\text{g})$ ,  $\text{CO}_2(\text{g})$ , and  $\text{H}_2\text{O}(\text{l})$ , respectively.<sup>16</sup>

The corresponding molar standard enthalpies of formation,  $\Delta_f H^\circ_{\text{m}}(\text{cr})$ , at 298.15 K for each monoadduct were derived taking into account the combustion reactions 1 and 2, the above-described standard enthalpies of combustion, and the molar standard enthalpies of formation of  $-393.15 \pm 0.13 \text{ kJ} \cdot \text{mol}^{-1}$  for  $\text{CO}_2(\text{g})$ <sup>16</sup> and  $-285.83 \pm 0.04 \text{ kJ} \cdot \text{mol}^{-1}$  for  $\text{H}_2\text{O}(\text{l})$ .<sup>16</sup> The results of the thermodynamics properties that were measured and derived from the combustion experiments of  $\text{C}_{61}(\text{COOEt})_2(\text{cr})$  and  $\text{C}_{71}(\text{COOEt})_2(\text{cr})$  are summarized in Table 3.

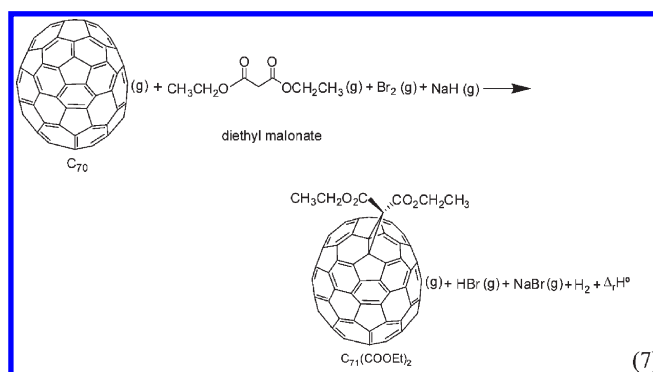
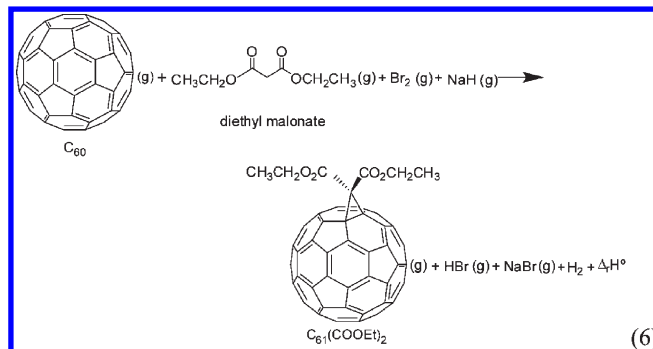
The dispersions associated with the mean values of the thermodynamic properties of the monoadducts in Table 3 are twice the overall uncertainties. These include dispersions from the calibration and the energies of combustion for cotton and Vaseline.<sup>17</sup> Table 3 shows that the uncertainties in the energy of combustion measurements were around 0.1% for the monoadducts of  $\text{C}_{60}$  and  $\text{C}_{70}$ , when employing the microcombustion technique and samples of less than 2 mg.

From the difference between the molar standard enthalpy of formation values for each monoadduct reported in Table 3 and the data of molar standard enthalpies of formation of  $2293.1 \pm 44.8$  and  $2537.4 \pm 37.4 \text{ kJ} \cdot \text{mol}^{-1}$  for  $\text{C}_{60}$  and  $\text{C}_{70}$ , respectively, measured also by the microcombustion technique here utilized,<sup>9b</sup> the enthalpic contributions by the functionalization of these fullerenes were calculated as follows:  $\Delta_{\text{funct}} H^\circ_{\text{m}}[\text{C}_{60}(\text{cr}) \rightarrow \text{C}_{61}(\text{COOEt})_2(\text{cr})] = -679.7 \pm 58.2 \text{ kJ} \cdot \text{mol}^{-1}$  and  $\Delta_{\text{funct}} H^\circ_{\text{m}}[\text{C}_{70}(\text{cr}) \rightarrow \text{C}_{71}(\text{COOEt})_2(\text{cr})] = -690.2 \pm 52.3 \text{ kJ} \cdot \text{mol}^{-1}$ . The dispersions associated with values of the enthalpic contribution and the molar standard enthalpy of  $\text{C}_{60}$  and  $\text{C}_{70}$  were calculated as twice the overall uncertainty.<sup>17a</sup> These results show that the insertion of the substituent into the fullerene had a stabilizing effect in both cases. Nevertheless, the enthalpic change produced by the insertion of the bis(ethoxycarbonyl)-methane group into a double bond in the  $\text{C}_{70}$  sphere to obtain  $\text{C}_{71}(\text{COOEt})_2$  was more exothermic than that produced when the same group was inserted into  $\text{C}_{60}$ . This finding suggests an additional stabilization of  $10.5 \text{ kJ} \cdot \text{mol}^{-1}$  for the formation of  $\text{C}_{71}(\text{COOEt})_2$  with respect to  $\text{C}_{61}(\text{COOEt})_2$ .

The molar standard enthalpies of formation for  $\text{C}_{61}(\text{COOEt})_2$  and  $\text{C}_{71}(\text{COOEt})_2$  determined in this work, in conjunction with the molar standard enthalpies of formation for  $\text{C}_{60}$  and  $\text{C}_{70}$ ,<sup>9b</sup> also allowed the calculation of the functionalization reaction enthalpies for the condensed phases of  $\text{C}_{60}$  and  $\text{C}_{70}$  to give the corresponding solid monoadducts. This calculation was carried out using Hess's law and Bingel's reaction,<sup>6a</sup> as shown in Figure 2. To calculate the enthalpies of the functionalization reactions, individual molar standard enthalpies of formation at 298.15 K were considered:  $2293.1 \pm 44.8 \text{ kJ} \cdot \text{mol}^{-1}$  for  $\text{C}_{60}$ ,<sup>9b</sup>  $2537.4 \pm 37.4 \text{ kJ} \cdot \text{mol}^{-1}$  for  $\text{C}_{70}$ ,<sup>9b</sup>  $-986.6 \pm 4.2 \text{ kJ} \cdot \text{mol}^{-1}$  for diethyl malonate,<sup>18</sup>  $-56.44 \pm 0.08 \text{ kJ} \cdot \text{mol}^{-1}$  for  $\text{NaH}$ ,<sup>19</sup>  $-361.41 \pm 0.42 \text{ kJ} \cdot \text{mol}^{-1}$  for  $\text{NaBr}$ ,<sup>19</sup> and  $-36.44 \pm 0.17 \text{ kJ} \cdot \text{mol}^{-1}$  for  $\text{HBr}$ .<sup>19</sup> The resulting enthalpies of the functionalization reactions were  $\Delta_f H^\circ_{\text{m}} = -34.5 \text{ kJ} \cdot \text{mol}^{-1}$  for  $\text{C}_{60}$  and  $\Delta_f H^\circ_{\text{m}} = -45.0 \text{ kJ} \cdot \text{mol}^{-1}$  for  $\text{C}_{70}$ . These results, which do not take into account any solvent effects, reveal that the reaction of  $\text{C}_{70}$  with diethyl malonate to give  $\text{C}_{71}(\text{COOEt})_2$  was energetically favored by about  $10.5 \text{ kJ} \cdot \text{mol}^{-1}$ , with respect to the reaction of  $\text{C}_{60}$  to give  $\text{C}_{61}(\text{COOEt})_2$ .

On the other hand, the theoretical gas-phase enthalpies of formation for the monoadducts studied at 298 K were derived from the calculated enthalpies of the functionalization reactions

of  $\text{C}_{60}$  and  $\text{C}_{70}$  to give  $\text{C}_{61}(\text{COOEt})_2$  and  $\text{C}_{71}(\text{COOEt})_2$ . Such enthalpies of reaction were calculated based on the Bingel's reaction, as described above, but with all reactants and products in the gas phase:



The optimized geometries and selected bond lengths, bond angles, and dihedral angles of  $\text{C}_{61}(\text{COOEt})_2$  and  $\text{C}_{71}(\text{COOEt})_2$  are shown in the Supporting Information.

The DFT electronic energies ( $\epsilon_0$ ), thermal corrections to the enthalpy ( $H_{\text{corr}}$ ), and Gibbs free energies ( $G_{\text{corr}}$ ) of the molecules participating in reactions 6 and 7 are given in the Supporting Information. From these values, the enthalpies of reaction,  $\Delta_r H^\circ$ , and Gibbs free energies of reaction,  $\Delta_r G^\circ$ , were computed as follows:

$$\Delta_r H^\circ(298 \text{ K}) = \sum (\epsilon_0 + H_{\text{corr}})_{\text{products}} - \sum (\epsilon_0 + H_{\text{corr}})_{\text{reactants}} \quad (8)$$

$$\Delta_r G^\circ(298 \text{ K}) = \sum (\epsilon_0 + G_{\text{corr}})_{\text{products}} - \sum (\epsilon_0 + G_{\text{corr}})_{\text{reactants}} \quad (9)$$

where  $H_{\text{corr}} = [H^\circ_{\text{M}}(298 \text{ K}) - H^\circ_{\text{M}}(0 \text{ K})] + \text{ZPE}$  and  $G_{\text{corr}} = H_{\text{corr}} - TS$ .

From the theoretical result of the heats associated with reactions 6 and 7, as well as the experimental gas-phase enthalpies of formation of  $2475.1 \pm 44.9 \text{ kJ} \cdot \text{mol}^{-1}$  for  $\text{C}_{60}$ ,<sup>9b</sup>  $2737.4 \pm 37.9 \text{ kJ} \cdot \text{mol}^{-1}$  for  $\text{C}_{70}$ ,<sup>9b</sup>  $-921.7 \pm 4.2 \text{ kJ} \cdot \text{mol}^{-1}$  for diethyl malonate,<sup>18</sup>  $30.91 \pm 0.11 \text{ kJ} \cdot \text{mol}^{-1}$  for  $\text{Br}_2$ ,<sup>19</sup>  $124.3 \pm 1.9 \text{ kJ} \cdot \text{mol}^{-1}$  for  $\text{NaH}$ ,<sup>19</sup>  $-36.44 \pm 0.17 \text{ kJ} \cdot \text{mol}^{-1}$  for  $\text{HBr}$ ,<sup>19</sup> and  $-143.93 \pm 2.09 \text{ kJ} \cdot \text{mol}^{-1}$  for  $\text{NaBr}$ ,<sup>19</sup> the gas-phase enthalpies of formation of  $\text{C}_{61}(\text{COOEt})_2$  and

**Table 4.** DFT Enthalpies of Reaction, Enthalpies of Formation, Gibbs Free Energies of Reaction, and Gibbs Free Energies of Formation for  $C_{61}(\text{COOEt})_2$  and  $C_{71}(\text{COOEt})_2$  (in  $\text{kJ} \cdot \text{mol}^{-1}$ )

	B3LYP/3-21G*	B3LYP/6-31G	B3LYP/6-31G*	experimental
$C_{60} \rightarrow C_{61}(\text{COOEt})_2(\text{g})$				
$\Delta_f H^\circ_m(\text{g}, 298.15 \text{ K})$	−211.4	−220.6	−210.5	
$\Delta_f G^\circ_m(\text{g}, 298.15 \text{ K})$	−190.9	−195.6	−194.3	
$\Delta_{\text{sub}} H_m(298.15 \text{ K})^a$				$248.4 \pm 5.0^a$
$\Delta_f H^\circ_m(\text{g}, 298.15 \text{ K})$	1673.3	1664.1	1678.5	$1861.8 \pm 37.9^b$
$C_{70} \rightarrow C_{71}(\text{COOEt})_2(\text{g})$				
$\Delta_f H^\circ_m(\text{g}, 298.15 \text{ K})$	−217.4	−223.17	−212.7	
$\Delta_f G^\circ_m(\text{g}, 298.15 \text{ K})$	−194.1	−207.0	−224.7	
$\Delta_{\text{sub}} H_m(\text{g}, 298.15 \text{ K})^a$				$280.7 \pm 5.6^a$
$\Delta_f H^\circ_m(\text{g}, 298.15 \text{ K})$	1930.2	1924.5	1938.6	$2127.9 \pm 37.4^b$
$\Delta_f H^\circ[C_{71}(\text{COOEt})_2(\text{g})] - \Delta_f H^\circ[C_{61}(\text{COOEt})_2(\text{g})]$	256.9	260.4	260.1	$266.1 \pm 53.2$

<sup>a</sup> Calculated from group contribution method (ref 20). <sup>b</sup>  $\Delta_f H^\circ_m(\text{g}) \text{ exptl} = \Delta_f H^\circ_m(\text{cr}) + \Delta_{\text{sub}} H_m$ .

$C_{71}(\text{COOEt})_2$  were derived as follows:

$$\begin{aligned} \Delta_f H^\circ[C_{61}(\text{COOEt})_2(\text{g}), 298 \text{ K}] \\ = \Delta_f H^\circ(298 \text{ K}) - \Delta_f H^\circ[\text{HBr}(\text{g})] - \Delta_f H^\circ[\text{NaBr}(\text{g})] \\ + \Delta_f H^\circ[\text{C}_{60}(\text{g})] + \Delta_f H^\circ[\text{diethyl malonate}(\text{g})] \\ + \Delta_f H^\circ[\text{Br}_2(\text{g})] + \Delta_f H^\circ[\text{NaH}(\text{g})] \end{aligned} \quad (10)$$

$$\begin{aligned} \Delta_f H^\circ[C_{71}(\text{COOEt})_2(\text{g}), 298 \text{ K}] \\ = \Delta_f H^\circ(298 \text{ K}) - \Delta_f H^\circ[\text{HBr}(\text{g})] - \Delta_f H^\circ[\text{NaBr}(\text{g})] \\ + \Delta_f H^\circ[\text{C}_{70}(\text{g})] + \Delta_f H^\circ[\text{diethyl malonate}(\text{g})] \\ + \Delta_f H^\circ[\text{Br}_2(\text{g})] + \Delta_f H^\circ[\text{NaH}(\text{g})] \end{aligned} \quad (11)$$

Values of  $\Delta_f H^\circ_m(\text{g})$ ,  $\Delta_f G^\circ_m(\text{g})$ , and  $\Delta_f H^\circ_m(\text{g})$  for  $C_{61}(\text{COOEt})_2(\text{g})$  and  $C_{71}(\text{COOEt})_2(\text{g})$ , as calculated from eqs 8–11 at the various levels of theory, are displayed in Table 4. The resulting gas-phase enthalpies and Gibbs energies of reaction show that the reaction of  $C_{70}$  with diethyl malonate to give  $C_{71}(\text{COOEt})_2(\text{g})$  was also slightly favored with respect to that of  $C_{60}$  to give  $C_{61}(\text{COOEt})_2(\text{g})$ . This reaction was favored by around 4.0 to 11.4  $\text{kJ} \cdot \text{mol}^{-1}$ , depending on the level of theory utilized. Therefore, both the experimental and theoretical results of  $\Delta_f H^\circ_m$  obtained in this work suggest that, in the solid and gas phases, functionalization on  $C_{70}$  was more exothermic than the equivalent process on  $C_{60}$ . This finding is consistent with results that have been recently reported, where the solid- and gas-phase reactions of  $C_{70}$  with 1-phenyl-1-(3-(methoxycarbonyl)propyl)diazomethane to yield 70PCBM were also found to be favored by 61  $\text{kJ} \cdot \text{mol}^{-1}$  with respect to that of  $C_{60}$  with the same functional group to give 60PCBM.<sup>8b</sup> In the current work, even that the difference in the heat of functionalization is around one-sixth of that found for the PCBMs, the trend is the same, insertion of the same functional group to releases more energy in the  $C_{70}$  with respect to the  $C_{60}$ .

These results are also in line with a recent theoretical study by DFT that have been carried out on  $C_{60}$  and  $C_{70}$ , which has shown that some of the  $C_{70}$  sites have larger reaction energies than for  $C_{60}$ .<sup>21</sup> Two of the three of these sites with greater reaction energies in  $C_{70}$  involve the C(8)–C(25) and C(9)–C(10)

bonds, and it is known that the monoadduct  $C_{71}(\text{COOEt})_2$  is an “ $\alpha$ -type” compound, being formed precisely by addition to the reactive double bond C(8)–C(25).<sup>10</sup>

On the other hand, for comparison of the theoretical  $\Delta_f H^\circ_m(\text{g})$  with the experimental one, accurate values of the molar standard enthalpies of sublimation at  $T = 298 \text{ K}$  for  $C_{61}(\text{COOEt})_2$  and  $C_{71}(\text{COOEt})_2$  are required; however, these values are not available in the literature. Therefore, these quantities were estimated using a group contribution method based on experimental data,<sup>20</sup> resulting  $\Delta_{\text{sub}} H_m(298 \text{ K}) = 248.4 \pm 5.0 \text{ kJ} \cdot \text{mol}^{-1}$  for  $C_{61}(\text{COOEt})_2$  and  $\Delta_{\text{sub}} H_m(298 \text{ K}) = 280.7 \pm 5.6 \text{ kJ} \cdot \text{mol}^{-1}$  for  $C_{71}(\text{COOEt})_2$  (see the Supporting Information). The uncertainty accompanying each of these values was calculated to be around 2.0% of the estimated heats of sublimation. From the molar standard enthalpies of formation and the enthalpies of sublimation, the gas-phase enthalpies of formation,  $\Delta_f H^\circ_m(\text{g})$ , for  $C_{61}(\text{COOEt})_2$  and  $C_{71}(\text{COOEt})_2$  were calculated to be  $1861.8 \pm 37.9$  and  $2127.9 \pm 37.4 \text{ kJ} \cdot \text{mol}^{-1}$ , respectively. Table 4 shows that the maximum differences between the experimental and theoretical enthalpies of formation were 197.7 and 203.4  $\text{kJ} \cdot \text{mol}^{-1}$  for  $C_{61}(\text{COOEt})_2(\text{g})$  and  $C_{71}(\text{COOEt})_2(\text{g})$ , respectively. Nevertheless, when the difference in the enthalpies of formation of  $C_{61}(\text{COOEt})_2(\text{g})$  and  $C_{71}(\text{COOEt})_2(\text{g})$  was calculated, an excellent agreement between the experimental and theoretical results was found (see last line in Table 4).

## 5. CONCLUSIONS

Microcombustion calorimetry was used to measure the energies of combustion for the Bingel-type monoadducts  $C_{61}(\text{COOEt})_2(\text{cr})$  and  $C_{71}(\text{COOEt})_2(\text{cr})$  with a precision better than 99.9%. This finding made it possible to derive precise values for the molar standard enthalpies of formation of these methanofullerenes, as well as the enthalpic contributions for functionalization and the molar standard enthalpies of reaction to produce the respective monoadducts. The resulting enthalpies of functionalization indicate that the insertion of the bis-(ethoxycarbonyl)methane group on  $C_{70}$  produces a more exothermic enthalpic change than that generated when the same substituent is inserted on  $C_{60}$ . The theoretical enthalpies of reaction at the level of theory B3LYP/6-31G\* also suggest that, in the gas phase, the reaction of  $C_{70}$  with diethyl malonate to yield

$C_{71}(\text{COOEt})_2(\text{g})$  is energetically favored over  $C_{61}(\text{COOEt})_2(\text{g})$ , thus producing an additional stabilization for the formation of  $C_{71}(\text{COOEt})_2(\text{g})$  with respect to  $C_{61}(\text{COOEt})_2(\text{g})$  which is supported by the theoretically estimated Gibbs reaction energies.

## ■ ASSOCIATED CONTENT

**S Supporting Information.** Tables with physical, chemical, and thermochemical properties required in standard state corrections, detailed mass and energy data involved in each calibration and combustion experiment, selected geometric parameters of each monoadduct as well as DFT electronic energies and thermal corrections, listing of group contributions for estimation of the enthalpies of sublimation for the Bingel's monoadducts, and  $^1\text{H}$  NMR spectra of each monoadduct demonstrating absence of solvent in the samples. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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