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Synthesis of an asymmetric fullerene dimer via sequential cycloadditions

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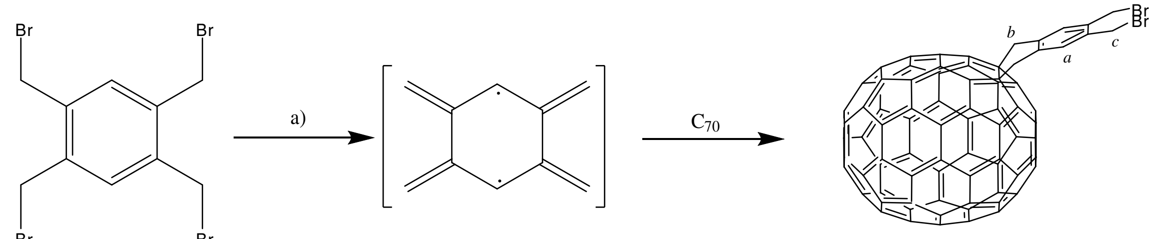
Abstract—A single isomer of a monofunctionalised C_{70} fullerene is isolated and characterised using variable temperature NMR spectroscopy. Pendant methylene bromide groups allow for further cycloaddition reactions and a C_{60}–C_{70} asymmetric fullerene dimer is thus prepared.

Fullerene dimers and multi-fullerene assemblies based on C_{60} units often possess interesting electronic properties such as a cooperative photophysical effect.[1,2] Few asymmetric fullerene dimers in which one carbon cage is C_{60} and the other C_{70} have been reported. To date, directly bonded C_{130}[3] and oxygen bridged $C_{130}O$[4] dimers have been prepared via mechanochemical solid-state reactions. Larger fullerenes such as C_{70} exhibit a greater degree of complexity during chemical reactions due to variable reactivity over the carbon surface and to the large number of possible isomers obtained in simple functionalisations.[5] Here, we report the preparation and characterisation of an asymmetric fullerene dimer by sequential cycloadditions using solution chemistry. A functionalised C_{70} intermediate is isolated as a single isomer and characterised by variable temperature NMR. Subsequent reaction with C_{60} yields an asymmetric dimer.

In a reaction analogous to previously reported work,[6] bis-*o*-quinodimethane and C_{70} were reacted in the presence of potassium iodide and 18-crown-6. HPLC of the product mixture revealed that the reaction yielded four isomers of the C_{70} monomer product (Scheme 1).[7] Separation and characterisation of these products revealed that a significant amount of oxidation had occurred during the synthesis and/or processing of the samples. The molecular ion peaks of two oxide-free isomers were observed by MALDI ionisation at *m*/*z* 1129.9. One isomer was present only in a low yield, so the second was purified and characterised with the potential for subsequent reactions.[8]



(1)

Scheme 1. Reaction of C_{70} with bis-*o*-quinodimethane (only one isomer shown). Reagents and condition: (a) KI, 18-crown-6, toluene, reflux.

Keywords: Fullerenes; Dimers; Cycloadditions.

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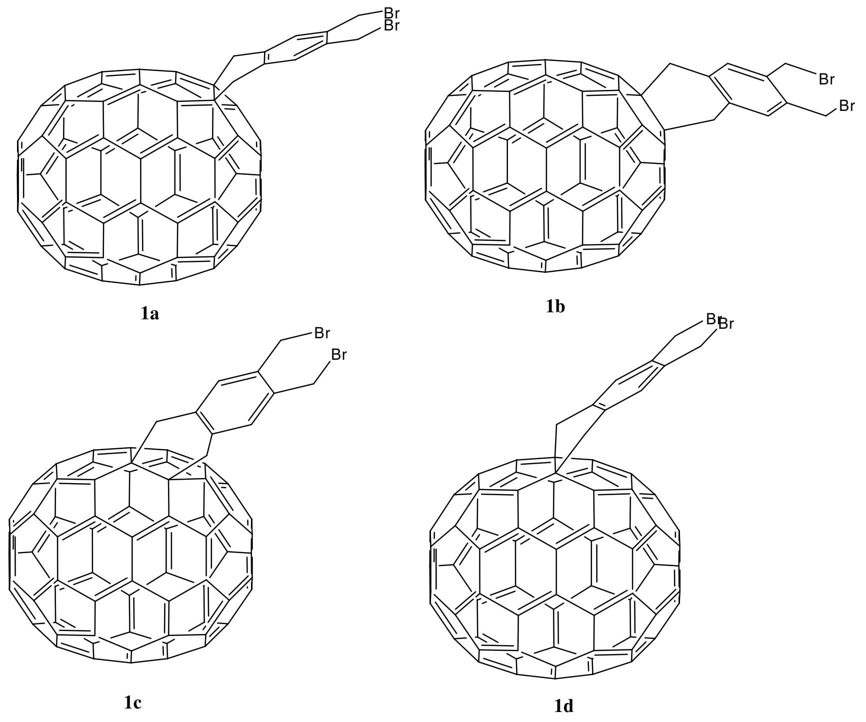


1a

1b

1c

1d

Figure 1. Structures of the four possible monoadducts of C_{70}.

Six-membered cyclohexene rings adjoining fullerene cages are commonly observed to interconvert between two boat conformations. Of the four possible isomers **1a–d** (Fig. 1), only two, **1b** and **1d**, undergo changes in symmetry (C_1 to C_s and C_s to C_{2v}) upon variation of exchange rates as a function of temperature.[9]

The variable temperature ^1H NMR (VT-NMR) of monomer **1** in toluene revealed four distinct proton resonances corresponding to the four protons of the cyclohexene ring. Increasing the temperature led to broadening of the resonances, followed by coalescence and the emergence of two sharp resonances as a result of rapid ring flipping on the NMR timescale (Fig. 2). This observation, coupled with the fact that isomer **1d** is rarely observed in analogous reactions due to lower equatorial reactivity, allows us to identify the product as isomer **1b**.

The analysis of the VT-NMR data reveals a coalescence temperature (T_c) of 300.4 K. The lifetime of exchange (τ) is calculated to be 3.52 and the energy barrier $\Delta G^\ddagger$ found to be 30.72 kJ mol^{-1}.

The presence of two methylene bromide groups allows for the subsequent reaction of the C_{70} monomer **1b** with C_{60} to produce an asymmetric dimer under conditions analogous to the initial functionalisation (Scheme 2).[10]

HPLC purification of the product mixture (Buckyprep-M, 18 ml min^{-1}) gave the asymmetric dimer in a 85% yield.[11] MALDI mass spectrometry revealed a molecular ion peak at *m*/*z* 1691.1, and an observed isotopic distribution which was in agreement with the theoretical isotopic distribution. ^1H NMR analysis in $CDCl_3/CS_2$ showed a peak at $\delta = 7.98$ ppm corresponding to the two aromatic protons. The four CH_2 groups were represented by four doublets between $\delta = 4.11$ and 4.60 ppm

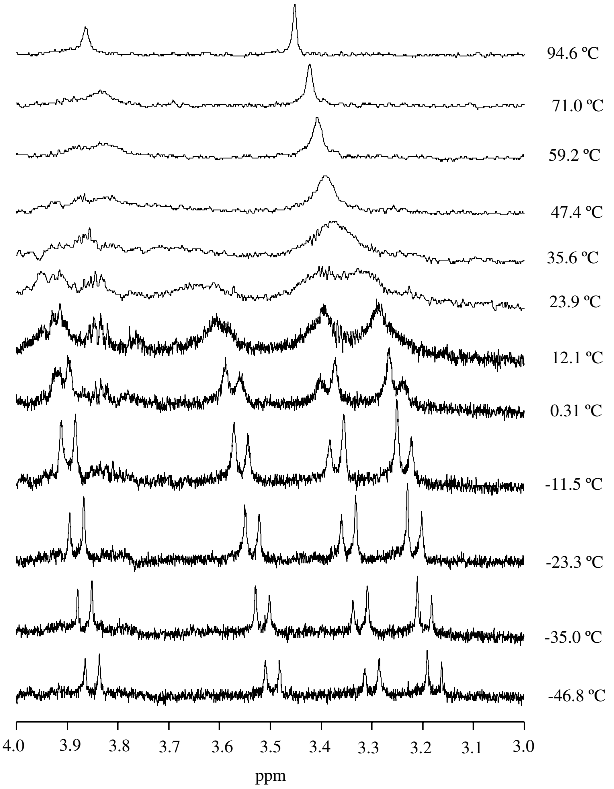
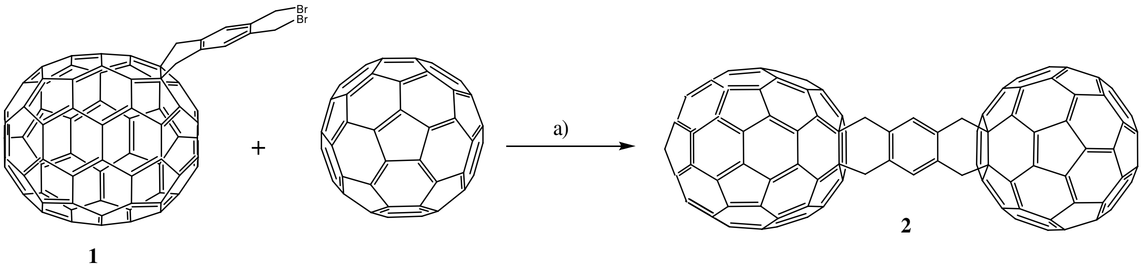


Figure 2. Variable temperature NMR of C_{70} monomer isomer **1b** (toluene-d_8). The pattern arises from ring flipping of the cyclohexene ring. Temperature calibrated using ethylene glycol.



Scheme 2. Synthesis of C_{60}/C_{70} asymmetric dimer **2** from C_{70} monomer isomer **1b**. Reagents and condition: (a) KI, 18-crown-6, toluene, reflux.

reflecting the asymmetry in the molecule, and a slow conformational change compared to the NMR timescale at this temperature. Poor solubility in toluene precluded the determination of physical data by VT-NMR.

A functionalised C_{70} species has been isolated as a single isomer and characterised by variable temperature NMR. Pendent reactive groups allowed for subsequent reaction with C_{60} in a second cycloaddition to produce a rare example of a C_{60}–C_{70} dimer.

Acknowledgements

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References and notes

1. Segura, J. L.; Martin, N. *Chem. Soc. Rev.* **2000**, *29*, 13.
2. Sánchez, L.; Herranz, M. A.; Martin, N. *J. Mater. Chem.* **2005**, *15*, 1409.
3. Komatsu, K.; Fujiwara, K.; Murata, Y. *Chem. Commun.* **2000**, 1583.
4. Eisler, H.-J.; Hennrich, F. H.; Werner, E.; Hertwig, A.; Stoermer, C.; Kappes, M. M. *J. Phys. Chem. A* **1998**, *102*, 3889.
5. Thilgen, C.; Hermann, A.; Diederich, F. *Angew. Chem., Int. Ed.* **1997**, *36*, 2268.
6. Belik, P.; Gügel, A.; Spickermann, J.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 78.
7. C_{70} (470 mg, 0.560 mmol), 1,2,4,5-tetrakis(bromomethyl)benzene (250 mg, 0.556 mmol), KI (100 mg, 0.602 mmol) and 18-crown-6 (600 mg, 2.27 mmol) were dissolved in toluene, and heated under reflux with stirring overnight in the dark under a nitrogen atmosphere. The product mixture was washed with 5% NaOH aqueous solution (150 ml) and water (150 ml) and dried over magnesium sulfate. After filtration, initial separation was carried out using HPLC (Buckyprep-M, 20 × 250 mm, 18 ml min^{-1}). Recycling of the monomer was required to purify each isomer present, with some subsequent recycling being carried out using a 5PBB column. C_{70} monomer (**1**) was isolated in a 27% yield (169 mg).
8. HPLC (Buckyprep-M, 20 × 250 mm, toluene, 18 ml min^{-1}) 8.64 min. MALDI *m*/*z*: 1129.9 M^- Calculated for $C_{80}H_{10}Br_2$ 1130.767. UV–vis λ(toluene)/nm 284 (ε/dm^3 mol^{-1} cm^{-1} 66,894), 310Sh (38,338), 344Sh (27,686), 400 (24,818), 464 (18,809), 538Sh (10,123). ^{1}H NMR (500 MHz, CS_2/$CDCl_3$) $\delta = 7.68$ (2H, s), 4.79 (2H, s), 4.72 (2H, s), 4.26 (1H, br s), 4.07 (1H, br s), 3.87 (1H, br s), 3.65 (1H, br s). ^{13}C NMR (125 MHz, CS_2/$CDCl_3$) $\delta = 151.1$, 151.1, 150.4, 149.6, 149.3, 149.2, 148.8, 148.6, 147.2, 146.8, 146.7, 146.1, 145.6, 142.9, 142.8, 142.7, 139.9, 137.9, 137.3, 136.1, 131.0, 130.0, 129.9, 128.8, 128.0, 125.1, 58.6, 57.0, 44.3, 40.7, 29.6, 29.6.
9. Hermann, A.; Diederich, F.; Thilgen, C. *Helv. Chim. Acta* **1994**, *77*, 1689.
10. C_{70} monomer **1b** (9.49 mg, 0.00840 mmol), C_{60} (24.2 mg, 0.0336 mmol), KI (2.50 mg, 0.0156 mmol) and 18-crown-6 (15 mg, 0.0568 mmol) were heated under reflux overnight in toluene (40 ml) under nitrogen in the dark with stirring. Solid deposited on the side of the flask was subsequently removed by sonication in toluene. The product mixture was washed with 5% NaOH solution (100 ml) and water (100 ml) and dried over magnesium sulfate. After filtration, separation was carried out by HPLC (Buckyprep-M, 20 × 250 mm, 18 ml min^{-1}).
11. HPLC (Buckyprep-M, 20 × 250 mm, toluene, 18 ml min^{-1}) 31.3 min. MALDI *m*/*z*: 1691.1 M^- Calculated for $C_{140}H_{10}$ 1691.619. UV–vis λ(toluene)/nm 284 (ε/dm^3 mol^{-1} cm^{-1} 93,820), 310 (61,296), 398 (26,706), 438Sh (18,925); ^{1}H NMR (500 MHz, CS_2/$CDCl_3$) $\delta = 7.98$ (2H, s), 4.60 (2H, d), 4.45 (2H, d), 4.28 (2H, d), 4.11 (2H, d).