The fullerene cross-dimer C_{130}: synthesis and properties

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The fullerene C_{60}–C_{70} cross-dimer C_{130} was synthesized by the mechanochemical solid-state reaction using a high-speed vibration milling technique, and was characterized by UV-vis and ^{13}C NMR spectroscopy as well as electrochemical methods.

The multiple [2 + 2] cycloadditions of C_{60} molecules afford the all-carbon C_{60} polymers by photo-irradiation[1] or high-pressure/high-temperature treatment of C_{60}.[2] However, it is rather difficult to control these reactions to give selectively the dimers and/or trimers. In contrast, it was demonstrated in our previous work that the fullerene dimer C_{120}[3] and trimer C_{180}[4] were successfully produced by the mechanochemical solid-state reaction using a high-speed vibration milling (HSVM) technique. So far there has been no report concerning the oligomerization of C_{70}.† In this paper we report the formation of a C_{60}–C_{70} cross-dimer, C_{130}, by the use of the solid-state HSVM reaction in the presence of 4-aminopyridine which proved to be an effective catalyst for the synthesis of C_{120}[3] and C_{180}.[4]

The reaction was conducted by placing C_{60} (23 mg, 0.032 mmol) and C_{70} (27 mg, 0.032 mmol) in a mixing capsule made of stainless steel, together with 4-aminopyridine (6.5 mg, 0.069 mmol) and a mixing ball, and treating them by HSVM for 30 min. The mixture was examined by HPLC on a Buckyprep column eluted with toluene. Although most of the mixture was found to be the starting materials, the formation of a small amount of what was possibly C_{130} was observed with a retention time of 24 min (HPLC peak area, 1.5%) in addition to C_{120} at 14.5 min (6%), unchanged C_{60} at 7.5 min (46%), and C_{70} at 12 min (44%).

The portion with an HPLC peak at the retention time of 24 min on a Buckyprep column was isolated by the use of a 5PBB column eluted with *o*-dichlorobenzene (ODCB). The analytical HPLC on a Buckyprep column showed that this is composed of a single isomer, and this was confirmed by the ^{13}C NMR spectrum (*vide infra*). The isolated fraction was found to undergo slow dissociation into C_{60} and C_{70} under room light with a half life of about 2 days, suggesting that this peak actually corresponds to C_{130}, which is the [2 + 2] cycloaddition product of C_{60} and C_{70}. The isolated yield of C_{130} was 3.0% (1.5 mg).

After treating this fraction with NaCN in ODCB–*N*,*N*-dimethylformamide, atmospheric pressure chemical ionization mass spectroscopy operated in the negative ion mode exhibited peaks at *m/z* 1586 and 1613 corresponding to the mono- and biscyanated C_{130}, *i.e.* $C_{130}(CN)^-$ and $C_{130}H(CN)_2{}^-$, respectively, thus proving the presence of C_{130} in this fraction.

The UV-vis spectrum‡ of C_{130} has the characteristic absorptions for C_{120} and also for the 1,2-dihydro[70]fullerene[5] as shown in Fig. 1. The ^{13}C NMR spectrum† of C_{130} (Fig. 2) clearly exhibits four signals for sp[3] carbons at 78.03, 75.75 (C_{60} carbons), 69.96, and 68.90 ppm (C_{70} carbons) and partially overlapped > 52 signals for the sp[2] carbons at 156.42–131.93 ppm, which corresponds to a structure with C_{60} and C_{70} connected by a shared cyclobutane ring with C_s symmetry. From these results, the most plausible structure of C_{130} is the one with a C_{60} cage attached at a 6–6 bond to a C_{70} cage at a 1,2-junction bond in a [2 + 2] fashion (Fig. 3). In fact, this isomer has been predicted to be more stable than the 3,4-isomer, in which the C_{70} cage is connected at the 3,4-junction bond.[6]

The redox behavior of C_{130} was examined by cyclic voltammetry and differential pulse voltammetry to give the voltammograms shown in Fig. 4. The curve with a dotted line is the voltammogram of a 1 : 1 mixture of C_{60} and C_{70}. It is clearly seen that the first reduction occurs at the same potential as the reduction potential of both C_{60} and C_{70}. The following three reduction waves are also identical to those of C_{60} and C_{70}. Therefore, it is quite likely that, as in the case of the C_{60} dimer,[3]

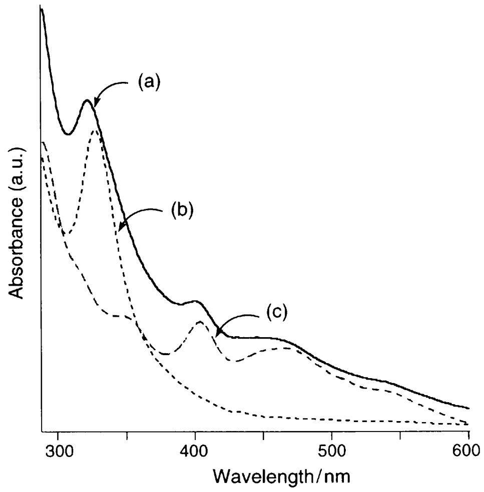

Fig. 1 UV-vis spectra of (a) C_{130} and (b) C_{120} in ODCB and (c) 1,2-H_2C_{70} in toluene–hexane (3 : 2).

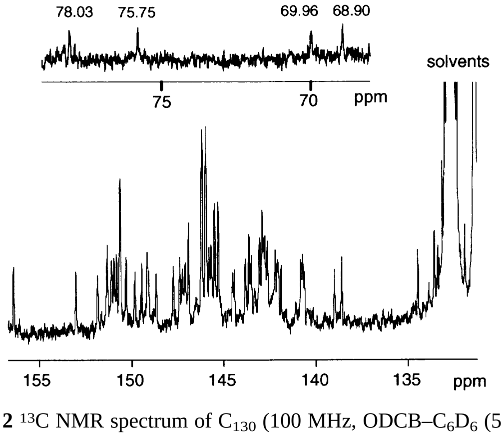

Fig. 2 ^{13}C NMR spectrum of C_{130} (100 MHz, ODCB–C_6D_6 (5 : 1)).

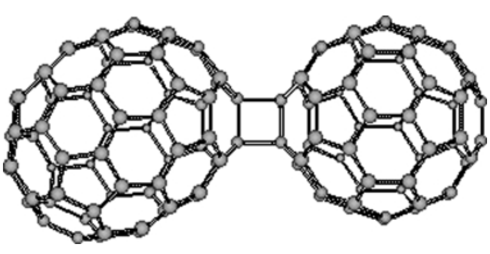

Fig. 3 PM3 calculated structure of C_{130}.

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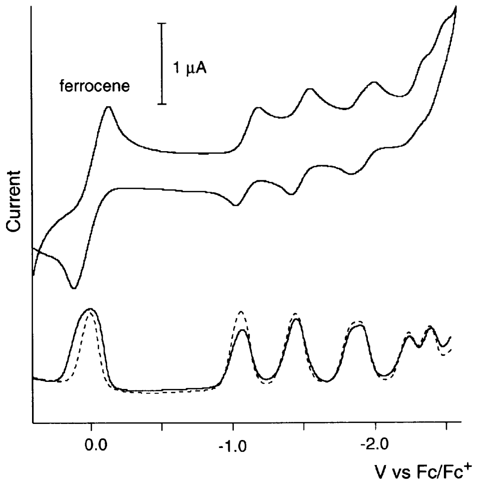

Fig. 4 Cyclic voltammogram (upper) and differential pulse voltammogram (lower) for C_{130} (a solid line) and a 1 : 1 mixture of C_{60} and C_{70} (a dotted line) measured in ODCB with 0.1 M $Bu_4N^+BF_4^-$: scan rate, 0.02 V s^{-1}.

the central intercage bonds are weak and are readily cleaved off to give radical anions of C_{60} and C_{70} upon obtaining extra negative charge.

Finally an attempt was made to dimerize C_{70} under the solid-state reaction conditions used to dimerize C_{60}, but absolutely no indication for such dimerization was observed. It is known that the most reactive 6–6 junction bond in a C_{70} molecule is the one at the '1,2' position.[7] The possibility of this bond in each C_{70} molecule encountering another is geometrically much lower than in the case of C_{60}, and this would be the reason for the poor reactivity of C_{70} towards dimerization.

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Notes and references

† **Note added in proof:**
A report has appeared on the high-pressure dimerization of C_{70}: S. Lebedkin, W. E. Hull, A. Soldatov, B. Renker and M. M. Kappes, *J. Phys. Chem. B*, 2000, **104**, 4101.

‡ λ_{max} (ODCB)/nm 323, 400, 462sh, 538sh; δ_C (100 MHz, ODCB-d_4) 156.42, 153.03, 151.85, 151.33, 151.10, 150.95, 150.82, 150.63, 150.30, 149.82, 149.45, 149.15, 149.08, 148.67, 147.74, 147.39, 147.25, 147.10. 146.92, 146.18, 145.97, 145.79, 145.69, 145.48, 145.30, 144.52, 144.44, 143.82, 143.63, 143.51, 143.07, 143.05, 143.00, 142.90, 142.83, 142.76, 142.63, 142.21, 142.10, 142.06, 142.03, 141.88, 140.83, 140.77, 140.70, 140.62, 138.99, 138.60, 134.47, 133.57, 133.15, 131.93, 78.03, 75.75, 69.96, and 68.90.

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