A new method for separating the D_3 and C_{2v} isomers of C_{78}†

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Received (in Gainesville, FL, USA) 13th May 2008, Accepted 10th September 2008
First published as an Advance Article on the web 27th October 2008
DOI: 10.1039/b808119k

A new chemical method has been applied to isolate isomers of C_{78}. The photochemical cycloaddition of a mixture of $C_{78}(D_3)$ and $C_{78}(C_{2v})$ with a disilirane affords only the mono-adduct of the C_{2v} isomer of C_{78}. Its counterpart does not give the mono-adduct with a disilirane. The D_3 isomer itself and the adduct of the C_{2v} isomer of C_{78} with a disilirane are easily separated by a HPLC procedure. A facile oxidative desilylation of the adduct takes place, resulting in the formation of pristine $C_{78}(C_{2v})$. In this context, the separation and isolation of the two isomers of C_{78} were successfully accomplished by using a silylation–oxidative desilylation process.

Introduction

The chemical reactivity of fullerenes has been systematically investigated over the past decade, providing us with a solid background towards the design and synthesis of novel and sophisticated derivatives of fullerenes.[1] Most studies have been focused on C_{60} and C_{70}, and research of the chemical reactivity of higher fullerenes has been very limited.[2] A reason for the scarcity of reports on the chemistry of higher fullerenes is that the isolation of single species of higher fullerenes has proved to be difficult due not only to their structural similarity, but also to their low abundance in soots, which requires their time-consuming and intensive HPLC separation. Recently, the isolation of pure isomers of C_{78}[3–5] and C_{84}[6–9] by HPLC separation has been reported. Up until now, there have been only limited reports on the chemical reactivity of C_{78}[10] and C_{84}[11–13] using isomeric mixtures. Although Diels–Alder[14] or Bingel/retro-Bingel[15] reactions have been applied to isolate the isomers of C_{84}, the results reveal that the isolation could not be effectively achieved because of a limited difference in reactivity toward those reactions among the isomers. The protocol of Bingel/retro-Bingel reaction takes advantage of the fact that covalent adducts of isomeric higher fullerenes are much easier to separate than their parent unfunctionalized spheroids, followed by changing the content ratio of the isomers. The separation of the isomers of C_{78}, in particular the cases of the C_{2v} and D_3 isomers, takes a long time by HPLC.[3,16] Due to the low solubility of C_{78} in HPLC solvents, it is not an adequate technique for the isolation of the C_{2v} and D_3 isomers on a quantitative scale. In the course of our studies on the chemical functionalization of fullerenes with organosilicon compounds, we found a difference in the photochemical reactivity of $C_{78}(D_3 + C_{2v})$ towards a disilirane,[17] which forced us to explore a new method for separating the two isomers of C_{78}.

We report here a new method for separating the two isomers of C_{78} that tackles the time-consuming HPLC separation problem.

Experimental

The soot-contained fullerenes were prepared by the Krätchmer–Hoffman arc discharge method.[18] The mixture of $C_{78}(C_{2v}$ and $D_3)$ was separated according to our recently developed method.[19] Electrochemical grade tetra-*n*-butylammonium perchlorate (TBAP), purchased from Wako Chemicals, was recrystallized from absolute ethanol and dried in a vacuum at 313 K prior to use. *o*-Dichlorobenzene (ODCB) was distilled over P_2O_5 under vacuum prior to use. UV-vis absorption spectra were recorded on a Perkin-Elmer Lambda 19 instrument. Positive ion fast atom bombardment (FAB) mass spectral data were obtained with a JEOL JMS-SX102A mass spectrometer using *m*-nitrobenzyl alcohol as the matrix.

Cyclic voltammetry and controlled potential bulk electrolysis in ODCB containing 0.2 M TBAP was carried out using a BAS CW-50. A conventional three electrode cell used for CV measurements consisted of a platinum working electrode, a platinum counterelectrode and a saturated calomel reference electrode (SCE). Controlled potential bulk electrolysis was performed using an "H" type cell, which consisted of two platinum gauze electrodes (working and counterelectrodes) separated by a sintered glass frit.

The reaction of C_{78} with 1,1,2,2-tetramesityl-1,2-disilirane

A mixture of $C_{78}(C_{2v})$ and $C_{78}(D_3)$ (2 : 1) was used as the starting material.[12] Irradiation of a toluene solution of

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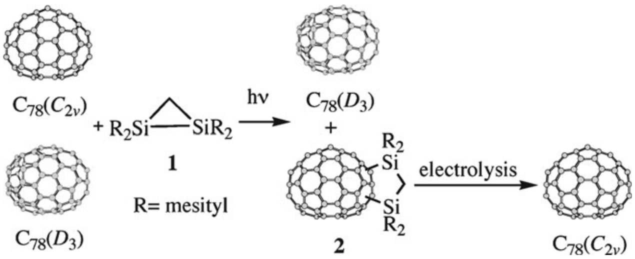
† Electronic supplementary information (ESI) available: Further HPLC profiles. See DOI: 10.1039/b808119k



Scheme 1

1,1,2,2-tetramesityl-1,2-disilirane (**1**, 1.6 equiv.) and $C_{78}(C_{2v} + D_3)$ with a halogen–tungsten lamp (cut off $<$ 400 nm) afforded 1,1,3,3-tetramesityl-1,3-disilolane (**2**) in 38% yield, with 33% of unreacted $C_{78}(D_3)$ remaining (Scheme 1). The reaction mixture was injected into a preparative gel permeation chromatography (GPC) column (JAIGEL 1H and 2H column) during the first stage to separate **2** and $C_{78}(D_3)$. The two pure adducts (**2a** and **2b**) were isolated by two-stage HPLC using a Buckyprep column (Nacalai Tesque), followed by a Buckyclutcher column (Regis Chemical).

$C_{78}(D_3)$. ^{13}C NMR (125 MHz, CD_3COCD_3/CS_2): δ 149.65, 148.35, 145.69, 144.72, 143.08, 142.03, 141.93, 141.11, 141.02, 140.66, 139.75, 133.15 and 132.39.

2a. UV/vis (CS_2): λ_{max} = 838, 744, 599 (sh), 555 (sh), 507 (sh) and 462 (sh) nm. ^{1}H NMR (300 MHz, $CDCl_3/CS_2$): δ 6.85 (s, 2H), 6.71 (s, 3H), 6.64 (s, 1H), 6.57 (s, 1H), 6.55 (s, 1H), 3.34 (s, 3H), 3.33 (s, 3H), 2.38 (s, 3H), 2.28 (s, 3H), 2.27 (s, 3H), 2.21 (s, 3H), 2.14 (s, 3H), 2.13 (s, 3H), 2.12 (d, J = 15.0 Hz, 1H), 2.09 (d, J = 15.0 Hz, 1H), 2.03 (s, 3H), 2.01 (s, 3H), 2.00 (s, 3H) and 1.96 (s, 3H). ^{13}C NMR (125 MHz, $CS_2/CDCl_3$): δ 164.69, 163.48, 154.62, 151.34, 149.43, 148.74, 148.24, 148.01, 147.60, 147.41, 147.00, 146.96, 146.90, 146.82, 146.61, 146.40, 145.92, 145.63, 145.60, 145.45, 145.33, 145.27, 145.22, 145.04, 145.00, 144.97, 144.75, 144.59, 144.37, 144.35, 144.09, 144.06, 144.03, 143.98, 143.92, 143.89, 143.63, 143.45, 143.36, 143.15, 142.96, 142.86, 142.74, 142.72, 142.68, 142.29, 142.11, 141.57, 141.44, 141.11, 141.06, 141.03, 141.01, 140.68, 140.40, 140.20, 140.12, 139.86, 139.82, 139.78, 139.63, 139.46, 139.40, 139.32, 139.28, 138.70, 138.38, 138.35, 137.83, 136.48, 135.70, 135.00, 134.88, 134.38, 134.13, 133.95, 133.09, 133.04, 132.73, 132.57, 132.14, 131.87, 131.81, 131.35, 131.16, 130.79, 130.40, 130.27, 130.22, 130.14, 130.07, 129.67, 128.21, 128.16, 65.26, 64.31, 28.79, 28.52, 25.57, 25.26, 25.19, 24.64, 23.50, 23.45, 21.14, 21.05, 21.00, 20.98 and 7.17. ^{29}Si NMR (100 MHz, $CS_2/CDCl_3$): δ −8.46 and −10.49. FAB-MS: m/z = 1486–1482.

2b. UV/vis (CS_2): λ_{max} = 883, 790 (sh), 748, 610, 560 and 502 nm. ^{1}H NMR (300 MHz, $CDCl_3/CS_2$): δ 6.87 (s, 2H), 6.72 (s, 1H), 6.70 (s, 1H), 6.64 (s, 1H), 6.61 (s, 1H), 6.54 (s, 1H), 6.53 (s, 1H), 3.47 (s, 3H), 3.41 (s, 3H), 2.51 (s, 3H), 2.35 (s, 3H), 2.29 (d, J = 14.5 Hz, 1H), 2.27 (s, 6H), 2.16 (s, 3H), 2.15 (d, J = 14.5 Hz, 1H), 2.12 (s, 3H), 2.11 (s, 3H), 2.06 (s, 3H), 2.02 (s, 3H) and 1.95 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3/CS_2$): δ 171.86, 157.40, 157.30, 153.29, 151.54, 150.56, 150.53, 149.50, 148.96, 148.91, 148.74, 148.50, 148.34, 148.04, 147.75, 147.73, 147.45, 147.37, 146.73, 146.60, 146.41, 146.37, 146.11, 146.06, 146.05, 146.00, 145.73, 145.57, 145.50, 145.40, 145.21, 144.94, 144.67, 144.41, 144.31, 144.15, 144.14, 144.09, 144.01, 143.94, 143.91, 143.76, 143.75, 143.64, 143.59, 143.54, 143.10, 142.80, 142.71, 142.41, 142.26, 142.07, 141.70, 141.07, 141.03, 141.00, 140.94, 140.61, 140.03, 139.72, 139.68, 139.65, 139.54, 139.35, 139.31, 138.58, 138.49, 138.38, 138.16, 138.13, 137.66, 137.23, 136.56, 136.03, 135.87, 135.28, 135.07, 134.79, 134.18, 134.15, 133.81, 133.71, 133.67, 132.97, 131.84, 131.81, 130.51, 130.46, 130.41, 130.32, 130.23, 130.03, 129.84, 129.55, 128.84, 128.77, 128.38, 128.09, 128.03, 66.23, 65.11, 29.01, 28.86, 26.04, 25.68, 25.56, 24.82, 23.58, 23.39, 21.01 and 9.20. ^{29}Si NMR (100 MHz, $CS_2/CDCl_3$): δ −8.51 and −11.28. FAB-MS: m/z = 1486–1482.

Separation of $C_{78}(C_{2v})$ and $C_{78}(D_3)$

Controlled potential bulk electrolysis of adduct **2** (a mixture of **2a**/**2b**), obtained from a photoreaction of **1** and $C_{78}(C_{2v}$ and $D_3)$, as mentioned above, was carried out by setting the applied potential at a value 140 mV more positive than the first oxidation potential of the adduct. Cyclic voltammetric measurements were carried out immediately after bulk electrolysis. After electrolysis, the solution was evaporated to remove ODCB under reduced pressure; the residue was then dissolved in CS_2. To remove the electrolyte, the resulting solution was passed through a short silica gel column. $C_{78}(C_{2v})$ was isolated by HPLC in 27% yield (based on starting C_{78}) (Fig. S-2†).

$C_{78}(C_{2v})$: ^{13}C NMR (125 MHz, CD_3COCD_3/CS_2): δ 147.89, 147.84, 147.26, 146.40, 146.32, 146.24, 145.27*, 145.17, 144.99, 144.77, 144.17, 143.62, 142.46*, 138.68 (×2), 138.36, 137.95, 136.77, 134.26, 132.91* and 132.59 (* indicates a half intensity signal).

Result and discussion

Irradiation of a toluene solution of the disilirane **1** and $C_{78}(C_{2v} + D_3)$ (2 : 1) afforded the disilolane **2** in 38% yield, with 33% unreacted C_{78} and 6% bis-adduct (Fig. S-1†). **2** and unreacted C_{78} were easily isolated by using a HPLC procedure. A HPLC analysis and the ^{13}C NMR spectrum of the unreacted C_{78} showed the existence of almost a single isomer, $C_{78}(D_3)$ (Fig. 1(b) and Fig. 2(b)). After a three-stage HPLC separation, two major isomers, **2a** and **2b**, were isolated in a pure form, accompanied by a trace amount of two other isomers, which were not further investigated. Mass spectrometry of both **2a** and **2b** displayed a peak at m/z = 1486–1482, as well as one for C_{78} at m/z 940–936, which arises from the loss of **1** from **2**. The UV-vis absorption spectra of **2a** and **2b** reveal that the spectra of the two isomers are very similar to each other.

Structural analysis of the two mono-adduct isomers was accomplished by ^{1}H and ^{13}C NMR measurements. The ^{1}H NMR spectrum of **2a** displayed 12 methyl signals of equal intensity between δ 1.9 and 3.5, and eight *meta*-proton signals of the mesityl groups between δ 6.4 and 7.0. An AB quartet (J = 3.7 Hz) for the two methylene protons was observed at δ 2.09 and 2.11. The ^{13}C NMR spectrum showed that adduct **2a** has a C_1-symmetry. Except for the peaks at δ 65.3 and 64.3,

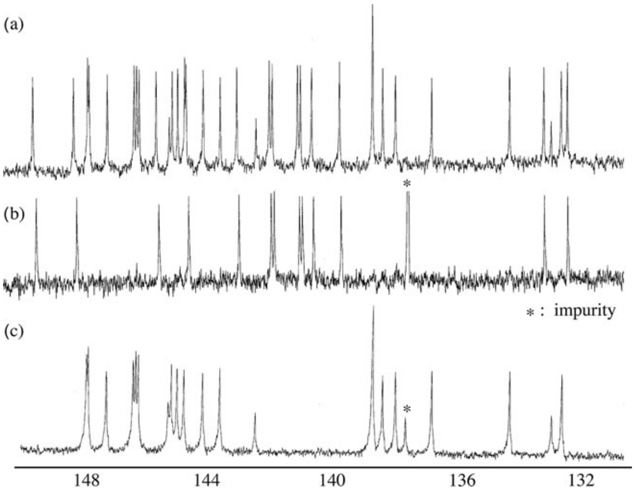


Fig. 1 ^{13}C NMR spectra of (a) the starting C_{78} (mixture of D_3 + C_{2v}), (b) unreacted $C_{78}(D_3)$ and (c) isolated $C_{78}(C_{2v})$ after oxidative desilylation.

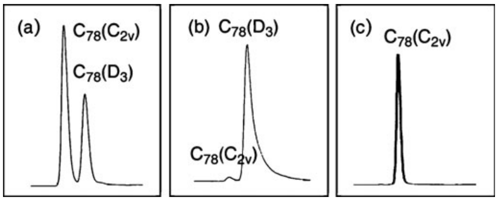


Fig. 2 The HPLC profiles of (a) $C_{78}(C_{2v} + D_3)$, (b) unreacted C_{78} and (c) C_{78} after oxidative desilylation.

assigned to the two bridgehead carbons, all of the other ^{13}C NMR signals of the fullerene cage appeared in the spectral range between δ 165 and 125. In the HMQC NMR spectrum, two cross-peaks due to the methylene protons at δ 2.09 and 2.11, and the methylene carbon atom of the disilirane component at δ 7.2 were observed. No change to the symmetry occurred below 120 °C. These spectral data suggest that cycloadduct **2a** has C_1 symmetry. The ^{1}H, ^{13}C, ^{29}Si, HMQC and HMBC spectra were also measured for **2b**. The results also indicate that **2b** has C_1 symmetry.

It is known that the disilirane **1** adds to C_{60} at the 6-6 ring junctions to afford the corresponding 5-membered ring.[20] It may therefore be assumed that **1** also adds to C_{78} at the 6-6 ring junctions. 21 sets of carbons and 18 distinct types of C–C bond at the 6-6 ring junctions are available in $C_{78}(C_{2v})$. Although 18 isomers are conceivable for **2**, interestingly, we isolated only two adducts, **2a** and **2b**, as major products in the reaction of C_{78} with **1**. Because **2a** and **2b** have C_1 symmetry, 11 isomers have to be considered. At this point, the exact assignment of the isomers must await an X-ray structural determination.

The fact that the adducts are formed upon irradiation at >400 nm, where C_{78} is the only light-absorbing component, indicates that the triplet state of C_{78} may interact with **1**, followed by an addition that is similar to that seen for C_{60}.[20]

To the shed light on the electronic properties,[21] the redox potentials of **2a** and **2b** were measured by means of differential pulse voltammetry. The data are collected in Table 1, together those of C_{60}, C_{78} isomers and the adduct of C_{60} with **1** (**3**)[20] as reference compounds. The salient feature is that **2b** has a low oxidation potential (+0.48 V) compared to C_{78} (+0.65 V) itself. On the other hand, the reduction potentials of **2a** and **2b** relative to C_{78} are cathodically-shifted, which indicates that the introduction of a silyl group results in reduced electron accepting properties. These findings are in agreement with those previously observed for other silylfullerenes.[21]

In order to obtain the C_{2v} isomer of C_{78}, we selected bulk controlled potential electrolytic oxidation to remove the silyl group from adduct **2**. Thus, the mixture of **2a** and **2b** was oxidized electrochemically in ODCB containing 0.2 M TBAP. After bulk electrolysis, a clear change in the CV indicated that a desilylation reaction had taken place, followed by the formation of $C_{78}(C_{2v})$. $C_{78}(C_{2v})$ was isolated in 27% yield (based on the starting C_{78} mixture) using a recycling HPLC system with a Buckyprep column. Fig. 1(c) and Fig. 2(c) show the ^{13}C NMR spectrum and the HPLC profile of the isolated $C_{78}(C_{2v})$, respectively. The ^{13}C NMR spectrum in Fig. 1(b) displays 13 signals of equal intensity, corresponding to the D_3 isomer. Meanwhile, Fig. 1(c) shows 21 signals, three of which have a half-intensity, corresponding to the C_{2v} isomer. On the basis of the difference in reactivity between the $C_{78}(C_{2v})$ and $C_{78}(D_3)$, we could successfully separate the two isomers by using a silylation–oxidative desilylation process, thus tackling the separation problem of these higher fullerenes.

Meanwhile, an interesting fact is that three isomers of C_{78} display different chemical reactivities in photochemical cycloaddition reactions with disiliranes. Our results reveal that only the C_{2v} isomer reacts with disiliranes, and the other two isomers (D_3 and C'_{2v}) do not react under the same conditions.

Table 1 Redox potentials[a] of C_{60}, **2a**, **2b**, **3** and C_{78} isomers

Compound	Ox_{E2}/V	Ox_{E1}/V	Red_{E1}/V	Red_{E2}/V	Red_{E3}/V	Red_{E4}/V
C_{60}		1.32	−1.13	−1.50	−1.94	−2.41
2a	0.92	0.67	−1.11	−1.40	−1.64	−2.00
2b		0.48	−1.27	−1.63	−2.02	−2.45
3[b]	1.23	0.73	−1.35	−1.70	−2.22	
$C_{78}(D_3)$		0.65	−0.76	−1.06	−1.79	−2.15
$C_{78}(C_{2v})$		0.88	−0.89	−1.22	−1.91	−2.27
$C_{78}(C'_{2v})$		0.67	−0.73	−1.17	−1.45	−2.22

[a] The values are in volts relative to the ferrocene/ferrocenium couple and were obtained by DPV. [b] Ref. 11. Conditions: 0.1 M $(n\text{-Bu})_4NPF_6$ in 1,2-dichlorobenzene. The working electrode and counterelectrode were Pt wire. Reference electrode Ag/0.01 M $AgNO_3$ and 0.1 M $(n\text{-Bu})_4NClO_4$ in CH_3CN. Pulse width 50 ms, pulse length 200 ms, scan rate 20 mV s^{-1}.

Up until now, there have been no reports of different reactivities among the isomers of higher fullerenes. Because C_{78} acts as an electron acceptor in the photochemical cycloaddition with disiliranes, the electronic properties of the three isomers may play a significant role in determining their reactivity.

To shed light on the electronic properties of the three isomers of C_{78} in the ground state, we measured their redox potentials by means of differential pulse voltammetry (Table 1). Comparing the redox potential of three isomers of C_{78}, the C_{2v} isomer is the most difficult to reduce of the three isomers. According to the electronic properties of the three isomers, it seems that the C_{2v} isomer has the lowest reactivity with respect to disiliranes among the three isomers. However, experimentally, only the C_{2v} isomer reacts with disiliranes. Therefore, the ground state electronic properties of the three isomers cannot explain their reactivity differences. Because we carried out a photochemical cycloaddition reaction in order to bis-silylate the three isomers of C_{78}, we should also consider the influence of their photophysical and photochemical properties in these reactions.

Conclusion

In conclusion, we have selectively silylated $C_{78}(C_{2v})$. The low photochemical reactivity of the D_3 isomer towards disiliranes is due to its photophysical properties. By utilizing the different photochemical reactivities of different isomers of C_{78}, we succeeded in quantitatively separating two of them, $C_{78}(C_{2v})$ and $C_{78}(D_3)$, using a silylation–oxidative desilylation procedure. The separation of different isomers of C_{78} by exploiting their differing reactivities might constitute an important stepping stone on the way to isolating other higher fullerenes.

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