Organic &
Biomolecular
Chemistry

Cite this: *Org. Biomol. Chem.*, 2011, **9**, 6646

www.rsc.org/obc

PAPER

Preparation and characterisation of an equatorial *para*-adduct of $(PhCH_2)HC_{70}$ from the reaction of C_{70}^{2-} with benzyl bromide and H_2O: addition effects in the polar and equatorial regions of C_{70}†

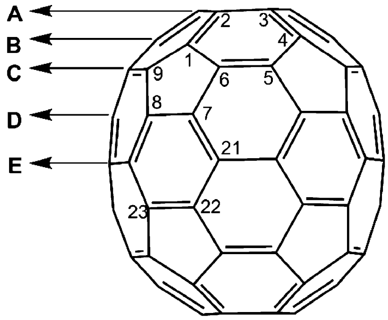
Ling Ni, Weiwei Chang, Hui-Lei Hou, Zong-Jun Li and Xiang Gao*

Received 24th May 2011, Accepted 8th July 2011
DOI: 10.1039/c1ob05809f

Benzyl(hydro)[70]fullerene regioisomers with the addends in both the equatorial and polar regions of C_{70} have been prepared *via* the reaction of dianionic C_{70} with benzyl bromide and H_2O. HRMS, UV-vis, ^1H, ^{13}C, HMQC (heteronuclear multiple quantum coherence) and HMBC (heteronuclear multiple bond coherence) NMR characterisations have shown that the addition in the equatorial region of C_{70} affords a new $(PhCH_2)HC_{70}$ regioisomer with *para*-positioned addends across a six-membered ring, which is different from the "polar" regioisomers where the addends have an *ortho*-addition pattern. ^1H NMR characterisations have shown a much stronger shielding effect for the addends in the equatorial region with respect to the counterparts in the polar region of C_{70}, while cyclic voltammetry study has shown a surprising positive shift for the first reduction potential of the equatorial regioisomer with respect to those of the polar regioisomer and pristine C_{70}, suggesting that the equatorial region of C_{70} is rather electropositive than electronegative. D_2O experiment has shown a significant difference of the deuterated product distribution between the equatorial and polar regioisomers, which can be justified by the different acidity of the $(PhCH_2)HC_{70}$ regioisomers. Computational calculations have been carried out to rationalize the formation of the $C_{70}HR$ regioisomers.

Introduction

Among the family of fullerenes, C_{70} is the second most abundant member and is the only fullerene in addition to C_{60} that can be obtained in macroscopic quantity for routine chemical and physical study.[1] Although both C_{60} and C_{70} have similar electronic structures by showing almost identical electrochemical properties,[2] and are capable of undergoing similar reactions,[3] the chemistry of C_{70} is much more complicated by the presence of five types of carbon atoms (Scheme 1) due to the low symmetry of the molecule,[3–5] and has still remained quite challenging. Notably, the organo[70]fullerenes have demonstrated a better performance as organic electronic materials than the C_{60} counterparts[6] probably due to the inherent difference of electronic structures, it is therefore of importance to explore more of the chemistry of C_{70}.



Scheme 1 Illustrated diagram of C_{70}. Partial numbering is taken from ref. 5. A, B, C, D, and E represent five different types of carbon atoms.

Previous work has shown that both C_{60} and C_{70} are readily reduced to anionic species by either electrochemical[7] or chemical methods,[8,9] which can be used to react with organic halides for further functionalizations.[7,8,9b] We have recently reported the reaction of C_{60}^{2-} with organic halides and H_2O, where 1,2-organo(hydro)[60]fullerenes are the major products instead of 1,4-diorgano[60]fullerenes,[10] which are usually the predominant products when H_2O is not involved in the reaction.[8,10] However, the reaction of C_{70}^{2-} with organic halides and H_2O has not been examined up to date. Herein, we report the reaction of C_{70}^{2-} with benzyl bromide and H_2O, where a novel $(PhCH_2)HC_{70}$ product with the *para*-addends in the equatorial region was isolated in addition to the previously reported $(PhCH_2)HC_{70}$ and $(PhCH_2)_2C_{70}$ products.[7b,11] Interestingly, the ^1H NMR has shown

---

State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Graduate School of Chinese Academy of Sciences, Chinese Academy of Sciences, 5625 Renmin Street, Changchun, Jilin, 130022, China. E-mail: xgao@ciac.jl.cn

† Electronic supplementary information (ESI) available: ^1H and ^{13}C NMR, MS, and HPLC of $H(PhCH_2)C_{70}$ regioisomers and 7,23-$(PhCH_2)_2C_{70}$, cyclic voltammograms of C_{70} and 7,23-$(PhCH_2)_2C_{70}$, and Cartesian coordinates, total energies and lowest frequencies of the reported stationary points for 1-$PhCH_2C_{70}^-$, 2-$PhCH_2C_{70}^-$, 5-$PhCH_2C_{70}^-$, 7-$PhCH_2C_{70}^-$, 21-$PhCH_2C_{70}^-$ intermediates and **2**, **4**, **5**, **6**, **7** obtained at B3LYP/6-31G level. See DOI: 10.1039/c1ob05809f

a much stronger shielding effect for the fullerenyl proton in the equatorial region with respect to that in the polar region of C_{70}, while the cyclic voltammetry has shown a positive-shifted reduction potential for the equatorial regioisomer with respect to the polar regioisomers and pristine C_{70}, suggesting a significant inherent difference between the equatorial and the polar regions of C_{70}.

Results and discussion

Synthesis and characterisation of 7,23-($PhCH_2$)HC_{70}

The reaction for the synthesis of 7,23-($PhCH_2$)HC_{70} was carried out in moisture DMF around 15 °C, and the procedures were similar to those reported previously for the synthesis of organo(hydro)[60]fullerenes.[10] At higher temperature, the compound was found to be unstable. Fig. 1 shows the HPLC trace of the crude products, where four fractions labeled as **P1** to **P4** were obtained along with unreacted C_{70}.

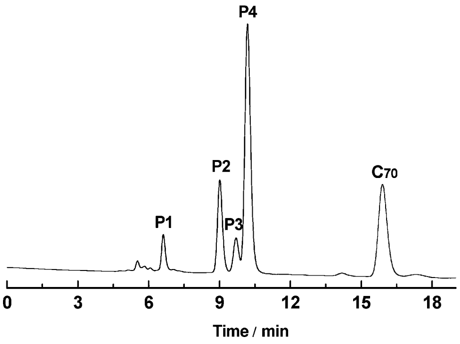


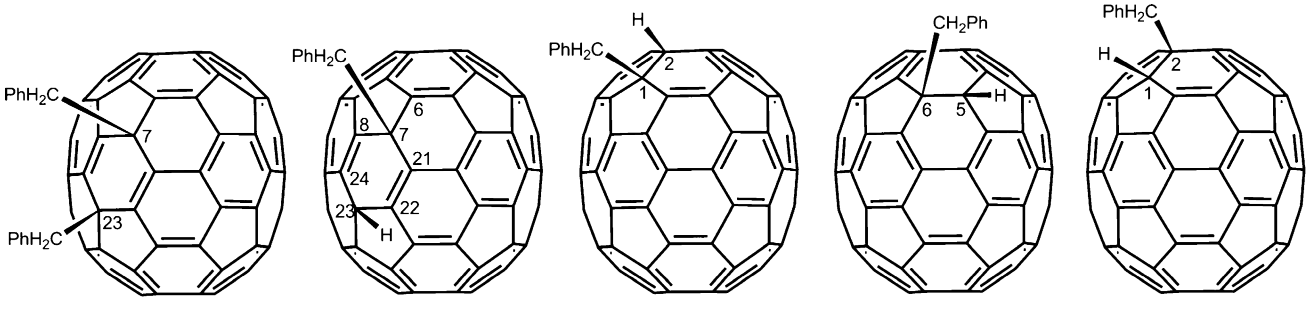
Fig. 1 HPLC trace of the crude reaction mixture of C_{70}^{2-} with benzyl bromide and H_2O in moisture DMF. The mixture was eluted with toluene over a semi-preparative Buckyprep column (20 × 250 mm) at a flow rate of 4.0 mL min^{-1} with detector wavelength set at 380 nm.

The structural identifications for **P1–P4** are achieved with the UV-vis, HRMS, and NMR characterisations. It is noteworthy that a considerable amount of toluene residue, which is from the HPLC purification of the products, is present in the NMR spectra of the products (see ESI for the NMR spectra†) even though the compounds were dried under vacuum for one or two days prior to the NMR measurements, suggesting the existence of strong interactions between the C_{70} derivatives and toluene, similar to the case reported recently for the singly bonded $PhCH_2C_{60}$–$C_{60}CH_2Ph$ dimer.[12] On the basis of the spectral characterisations (see ESI†) and comparison with the literature results,[7b,11] it shows that fraction **P1** is 7,23-$(PhCH_2)_2C_{70}$ (**1**), **P3** consists of a mixture of 1,2-($PhCH_2$)HC_{70} (**3a**) and 5,6-H($PhCH_2$)C_{70} (**3b**), and **P4** corresponds to 1,2-H($PhCH_2$)C_{70} (**4**) as shown in Scheme 2. It is interesting to find that fraction **P2** consists of a novel product, in which the benzyl and H-atom are placed at the 7,23-positions. C_{70} derivatives with such an addition pattern have been reported in literature,[13] however, to the best of our knowledge, the compound is the first example of C_{70} monoadduct with the H-atom and the organo group positioned with a *para*-addition pattern. Such a *para*-addition involving a small hydrogen atom has been previously observed for 1,4-H(*t*-Bu)C_{60}, however, the compound is very unstable and transformed into 1,2-H(*t*-Bu)C_{60} quickly.[14] Stable fullerene derivatives with the *para*-addition of hydrogen atom are reported for multiple-adducts such as hydrogenated diaryldihydropyridazine C_{60}[15] and $C_{70}H_8$,[9a] and the stability of such configuration in fullerene multiple adducts is likely due to the cooperative effects of the multiple addends.

The negative ESI FT-ICR MS (electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry) of **P2** shows the monoisotopic $[M - H]^-$ at 931.05629, which agrees well with the theoretical value of 931.05478, indicating that the compound has a formula of H($PhCH_2$)C_{70}. The UV-vis spectrum of **P2** is essentially the same as that of **P1** (see Figure S1†), indicating that **P2** has the same addition pattern as that of 7,23-$(PhCH_2)_2C_{70}$, since the UV-vis absorptions of C_{70} adducts are more characteristic of the addition patterns rather than the variance of the addition appendages.[9b,11b,16] Therefore, **P2** is tentatively identified as 7,23-($PhCH_2$)HC_{70} based on the HRMS and UV-vis spectroscopy.

The structure of **P2** is further characterized with NMR spectroscopy (recorded in CS_2 with acetone-d_6 as the external lock, see Figure S2†). The ^{1}H NMR of the compound shows an AB quartet centered at 2.96 ppm (ABq, $\Delta\nu_{AB}$ = 94 Hz, J_{AB} = 12.6 Hz) due to the methylene protons, and a singlet at 2.79 ppm arising from the fullerenyl proton. Resonances in the aromatic region are also observed, confirming the presence of the benzyl group in the molecule. The appearance of an AB quartet indicates that the methylene protons are diastereotopic to each other, implying that the added benzyl groups are not in the symmetry plane of the molecule.[17]

The ^{13}C NMR of **P2** (recorded in CS_2 with DMSO-d_6) exhibits three sp^3 resonances at 56.88, 46.46 and 44.66 ppm. The DEPT (distortionless enhancement by polarization transfer) HMQC



1 (P1) **2 (P2)** **3a (P3)** **3b (P3)** **4 (P4)**

Scheme 2 Illustrated structures of C_{70} derivatives obtained from the reaction of C_{70}^{2-} with benzyl bromide and water in DMF.

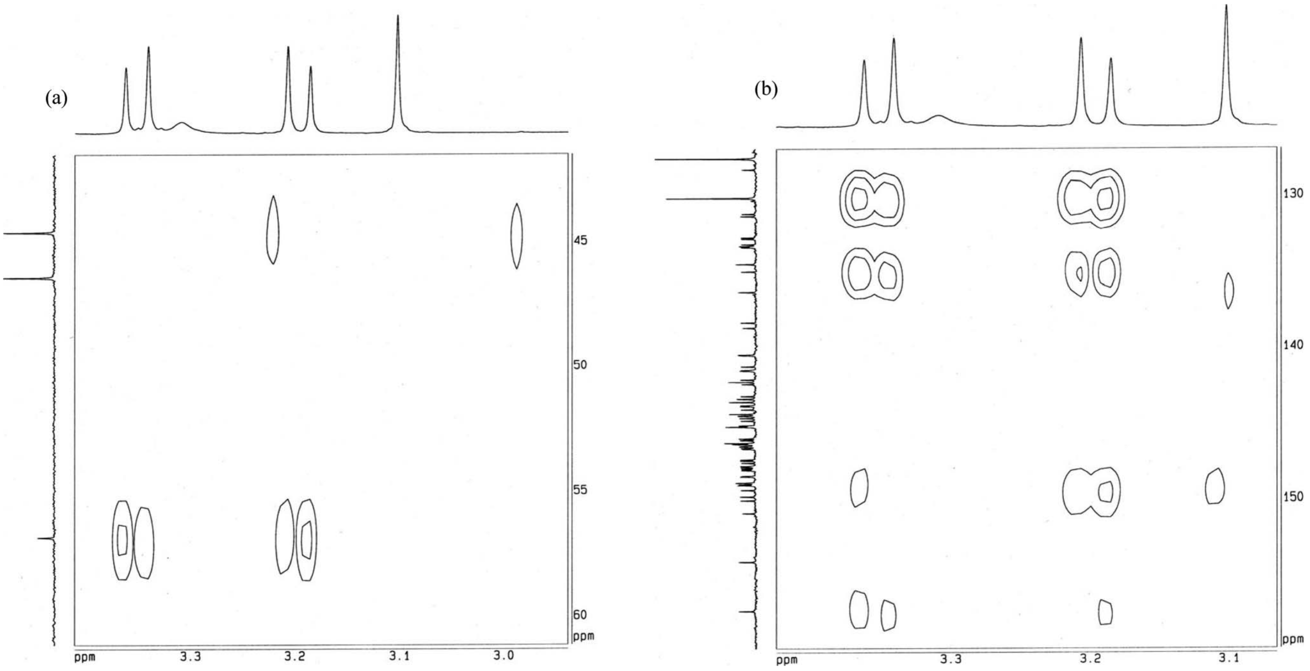


Fig. 2 Expanded HMBC NMR spectrum of **P2** recorded in CS_2 with DMSO-d_6 as the external lock. (a) Correlations with the sp^3 carbon atoms. (b) Correlations with the sp^2 carbon atoms.

NMR spectrum shows two cross peaks, one is between the fullerenyl proton and the carbon resonance at 44.66 ppm and the other is between the methylene quartet and the carbon resonance at 46.46 ppm. The results show unambiguously that the resonance at 46.46 ppm is due to the benzylic carbon atom, while the resonances at 56.88 and 44.66 ppm correspond to the C_{70} carbon atoms bonded to the benzyl group and the fullerenyl hydrogen respectively. As for the sp^2 region, it shows a total of 63 C_{70} carbon atoms from 157.4 to 131.2 ppm, along with four resonances from 134.6 to 126.6 ppm for the phenyl carbons. The result confirms that **P2** is a C_{70} monoadduct with C_1 symmetry. Further structural assignment is obtained with the HMBC NMR, since it is possible to identify the connectivity of the C_{70} carbon atoms adjacent to the appendages by showing the two-bond and three-bond hydrogen-carbon ($^2J_{CH}$ and $^3J_{CH}$) correlations.[18]

Fig. 2 shows the expanded HMBC spectrum of **P2** recorded in CS_2 with DMSO-d_6 as the external lock, and several important features are revealed. First, in the sp^3 carbon region (Fig. 2a), there is no correlation between the methylene protons (AB quartet) and the fullerenyl carbon atom (44.66 pm), and neither is there a correlation between the fullerenyl proton and the sp^3 C_{70} carbon atom bonded to the benzyl group (56.88 ppm), indicating the missing of the $^2J_{CH}$ couplings between the fullerenyl proton and the sp^3 C_{70} carbon atom bonded to the benzyl group, and also the absence of the $^3J_{CH}$ couplings between the benzylic protons and the fullerenyl carbon atom.[18,19] This provides important information that the two addends are not positioned adjacently with the *ortho*-position. The exhibited correlation between the AB quartet and the carbon resonance at 56.88 ppm is due to the $^2J_{CH}$ couplings between the methylene protons and the C_{70} carbon atom bonded to the benzyl group, consistent with the formation of the C_{70}–CH_2Ph bond. Notably, the cross peaks involving the carbon atom at 44.66 ppm do not line up with any protons, and they are likely due to the artifacts.

Fig. 2b shows the HMBC spectrum with the correlations in the sp^2 region. The most important feature is that both the benzylic protons and the fullerenyl proton are correlated with the same carbon atoms resonating around 150 ppm, which provides the key evidence that the benzyl and H-atom are positioned across a six-membered ring of C_{70} with a *para*-position, since both C8 and C21 (Scheme 2) can be simultaneously correlated with the methylene and fullerenyl protons *via* $^3J_{CH}$ couplings. In addition, it is noteworthy that the most downfield carbon atom is correlated with the methylene protons, which is likely due to the $^3J_{CH}$ couplings between C6 (Scheme 2) and the methylene protons, consistent with the previous results on C_{60} derivatives that the sp^2 fullerene carbon atoms located immediately adjacent to the fullerene sp^3 carbons are the ones with the most downfield resonance.[20]

^{1}H NMR of $H(PhCH_2)C_{70}$ regioisomers and strong shielding in the equatorial region

The ^{1}H NMR chemical shifts of the addends can be used as an external probe for the local aromaticity and ring currents of fullerenes and fullerene hexaanions.[21] The availability of 7,23-$(PhCH_2)HC_{70}$ is of interest since it is possible to compare the ^{1}H NMR resonances of the equatorial and polar regioisomers of $H(PhCH_2)C_{70}$, which may reveal the regional difference over the C_{70} molecule surface. Table 1 lists the chemical shifts for the fullerenyl and methylene protons of the obtained $H(PhCH_2)C_{70}$ regioisomers recorded in $CS_2/CDCl_3$ along with literature values recorded in the same solvent.

As is shown in Table 1, an increased shielding effect is observed for the fullerenyl hydrogen and the benzylic protons as the addends move from the polar to the equatorial region of C_{70}. Generally, the fullerenyl proton is more deshielded than the benzylic protons as shown by the three 2,1-, 1,2- and 5,

Table 1 Chemical shifts for the fullerenyl and methylene protons of $H(PhCH_2)C_{70}$ regioisomers recorded in $CS_2/CDCl_3$

	$H(PhCH_2)C_{70}$ Regioisomers			
δ (ppm)	2,1-$H(PhCH_2)C_{70}$	1,2-$H(PhCH_2)C_{70}$	5,6-$H(PhCH_2)C_{70}$	7,23-$(PhCH_2)HC_{70}$
H–C_{70}[a]	5.01	4.50	4.65	3.40
H–C_{70}[b]	5.06	4.56		
H_2–CPh[a]	3.77	4.07	3.72	3.55
H_2–CPh[b]	3.82	4.12		

[a] This work. [b] Taken from ref. 11b.

6-$H(PhCH_2)C_{70}$ regioisomers, probably due to the greater electron-withdrawing effect experienced by the fullerenyl proton since it is directly bonded to the fullerene cage. It is however noteworthy that for 7,23-$(PhCH_2)HC_{70}$, not only are the fullerenyl and benzylic hydrogens more shielded with respect to those of the other three regioisomers, but also the fullerenyl hydrogen is even more shielded than the benzylic protons (3.40 ppm *vs.* 3.55 ppm), implying that the equatorial region of C_{70} is rather electron-donating than electron-withdrawing. The observed strong shielding in the equatorial region is in agreement with the more aromatic nature of the equatorial hexagons,[22] and is consistent with recent ^1H NMR characterisations on an equatorial $C_{71}H_2$ product.[23]

Cyclic voltammetry of 1,2-$H(PhCH_2)C_{70}$ and 7,23-$(PhCH_2)HC_{70}$

The electrochemistry of organofullerene regioisomers has been a subject of intense interest since it may show pure addition effect on the electronic structural changes of fullerenes.[17,24] Fig. 3 shows the cyclic voltammograms of 1,2-$H(PhCH_2)C_{70}$ and 7,23-$(PhCH_2)HC_{70}$ recorded in PhCN containing 0.1 M TBAP (tetra-n-butylammonium perchlorate) with a scan rate of 0.1 V/s. Four reduction peaks with $E_{1/2}$ at –0.57, –0.96, –1.34, and –1.79 V *vs.* SCE are observed in the cyclic voltammogram of 1,2-$H(PhCH_2)C_{70}$. However, only the first three reductions are likely associated with the 1,2-$H(PhCH_2)C_{70}$, since the oxidation wave at E_{pa} = –0.53 V corresponding to 1,2-$H(PhCH_2)C_{70}^-$/1,2-$H(PhCH_2)C_{70}$ is missing when the scan is reversed from the fourth reduction. Previous work on the electrochemistry of fullerene hydrides has shown that the fullerenyl proton can be removed when the compound is reduced.[12,25] It is therefore likely that the observed redox wave at –1.79 V is associated with 2-$PhCH_2C_{70}^{3-}$/2-$PhCH_2C_{70}^{4-}$. Compared with the reduction potentials of C_{70} under the same conditions ($E_{1/2}$: –0.45, –0.85, –1.30, and –1.72 V *vs.* SCE, Figure S26†), a negative potential shift is observed for the reduction of 1,2-$H(PhCH_2)C_{70}$, which is consistent with the general behaviors observed for fullerene adducts due to the cleavage of the electronegative π-electron conjugation of fullerenes.[26]

The cyclic voltammogram of 7,23-$(PhCH_2)HC_{70}$ indicates that the anionic species of the compound is quite unstable, and it starts to decompose after it acquires one electron. The compound exhibits an irreversible first redox process with the E_{pc} at –0.41 V, and three subsequent quasi-reversible redox processes with $E_{1/2}$ at –0.94, –1.40, and –1.89 V *vs.* SCE, which are likely to be related to the intermediate of anionic 7-$PhCH_2C_{70}$ species due to the reductive loss of H.[12,25]

It is noteworthy that the reduction potential of 7,23-$(PhCH_2)HC_{70}$ is not only positively shifted with respect to that of 1,2-$H(PhCH_2)C_{70}$, but also even more positive than that of the parent C_{70} (E_{pc}^{1st} = –0.49 V, Figure S26†), which is in the contrary to the typical cathodic shift observed for the reduction potentials of fullerene derivatives with respect to those of pristine fullerenes, due to the cleavage of the electron-withdrawing π–conjugations.[26] The results therefore suggest that the equatorial region of C_{70} is rather electropositive than electronegative. The addition of the addends in the equatorial region cleaves the electropositive π-electron conjugation, and may thus increase the overall electronegativity of the molecule, causing a positive shift of the reduction potential. The observed electropositive property in the equatorial region of C_{70} from electrochemical measurement is consistent with the ^1H

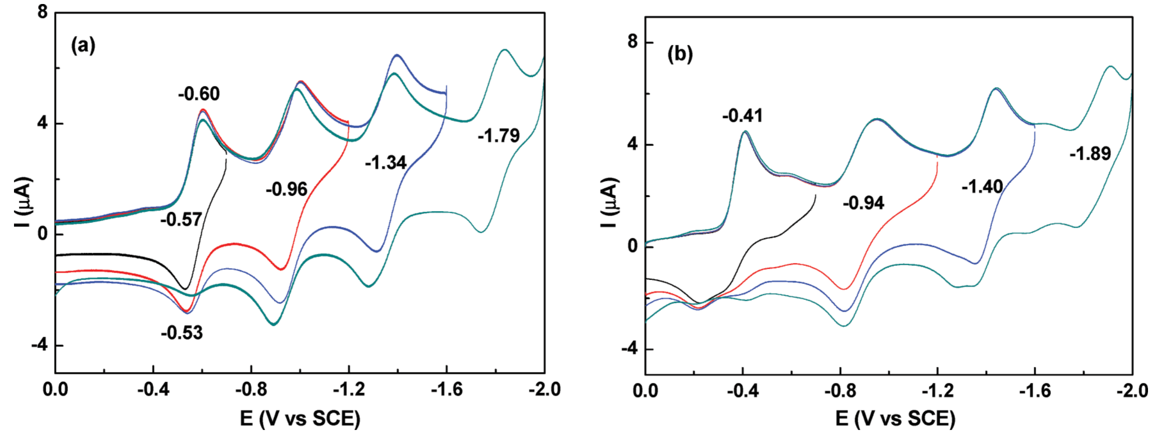


Fig. 3 Cyclic voltammograms of (a) 1,2-$H(PhCH_2)C_{70}$, and (b) 7,23-$(PhCH_2)HC_{70}$. Measurements were performed in benzonitrile solution containing 0.1 M TBAP at a scan rate of 0.1 V/s.

NMR data, where the fullerenyl proton in the equatorial region is even more shielded than the benzylic protons as shown in Table 1.

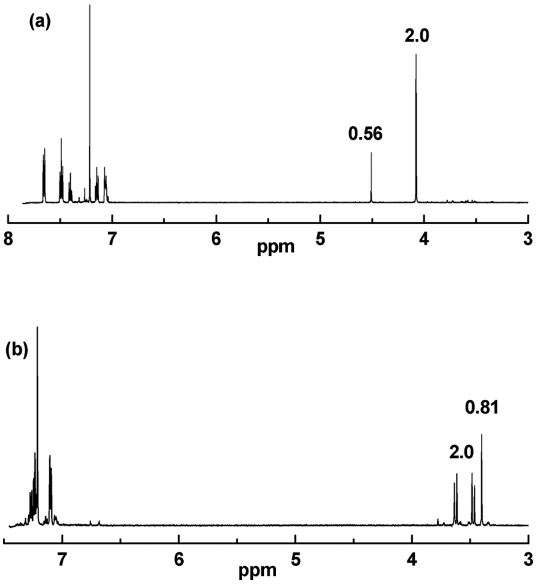


Fig. 4 ^{1}H NMR spectra of partially deuterated (a) 1,2-H($PhCH_2$)C_{70}, and (b) 7,23-($PhCH_2$)HC_{70} obtained from the reaction of C_{70}^{2-} with $PhCH_2Br$ in D_2O-containing DMF solution. The spectra were recorded in CS_2/$CDCl_3$. The number in the spectra refers to the relative integration area.

Origin of the fullerenyl hydrogen and different D_2O effects on the formation of 7,23-($PhCH_2$)HC_{70} and 1,2-H($PhCH_2$)C_{70}

Previous work on the formation of organo(hydro)[60]fullerenes has shown that the fullerenyl proton may originate from the H_2O residue in the reaction system.[10,27] It is therefore rational to assume that the fullerenyl hydrogen atoms for the obtained ($PhCH_2$)HC_{70} regioisomers are also from H_2O due to the similar reactivity of C_{60}^{2-} and C_{70}^{2-}. The reaction of C_{70}^{2-} with benzyl bromide leads to the formation of a series of ($PhCH_2$)$_2C_{70}$ regioisomers in dry PhCN solvent,[7b] while ($PhCH_2$)HC_{70} regioisomers were produced as shown in the HPLC after adding a small amount of water to freshly distilled PhCN (Figure S25†), confirming that the fullerenyl hydrogen is from water as the case for 1,2-($PhCH_2$)HC_{60}.[10]

Further experiment with the addition of D_2O confirms the source of fullerenyl proton is H_2O, and it shows a different H/D effect on the formation of 7,23-($PhCH_2$)HC_{70} and 1,2-H($PhCH_2$)C_{70}. Fig. 4 shows the ^{1}H NMR of the 1,2-H($PhCH_2$)C_{70} and 7,23-($PhCH_2$)HC_{70} obtained from the deuterated reaction, which was carried out in 50 mL of freshly distilled DMF solution, into which 100 µL of D_2O was added.

The integration area ratio of fullerenyl proton to methylene protons is 1 : 2 as expected for the product obtained in routine DMF (Figure S10†), while the ratio goes to 0.56 : 2 for the fraction obtained from D_2O-containing DMF, indicating that about 44% of the fullerenyl hydrogen is replaced by deuterium, which is comparable to the result obtained for 1,2-($PhCH_2$)HC_{60} under similar conditions,[10] demonstrating a reactivity similarity between the C_{70} polar region and C_{60}. However, the situation is quite different for 7,23-($PhCH_2$)HC_{70}. The integration area ratio of the fullerenyl hydrogen to the methylene protons is 0.94 : 2 as shown in the ^{1}H NMR of 7,23-($PhCH_2$)HC_{70} obtained from routine DMF (Figure S2†), while it changes to 0.81 : 2 as shown in Fig. 4b for the fraction of 7,23-($PhCH_2$)HC_{70} obtained from D_2O-containing DMF. The result shows a roughly only 15% intensity decrease of the fullerenyl hydrogen resonance for 7,23-($PhCH_2$)HC_{70} due to the deuterium replacement, which is significantly lower than that for 1,2-H($PhCH_2$)C_{70}. Such a difference is likely due to the acidity difference of the H–C_{70} between the 1,2-H($PhCH_2$)C_{70} and 7,23-($PhCH_2$)HC_{70} regioisomers. The pK_a of the two isomers were therefore evaluated with the electrochemical methods, which have been shown to be effective for measuring the acidity of fullerene hydrides,[28] to rationalize the difference of the D_2O experiment.

Fig. 5 shows the differential pulse voltammetry (DPV) measurements of the 1,2-H($PhCH_2$)C_{70} and 7,23-($PhCH_2$)HC_{70} regioisomers without and with the addition of sodium acetate (NaAc). As is shown in Fig. 5, the addition of 1.3 equivalent of acetate to 1,2-H($PhCH_2$)C_{70} resulted in a significant decrease of its first reduction peak, implying that 1,2-H($PhCH_2$)C_{70} is more acidic than acetic acid (pK_a = 4.75 in aqueous solution), which are quite typical for many C_{60} hydrides;[28] however, the addition of 1.3 equivalent of acetate into 7,23-($PhCH_2$)HC_{70} does not cause any significant decrease of its first reduction peak, suggesting that 7,23-($PhCH_2$)HC_{70} is much less acidic than acetic acid. The results

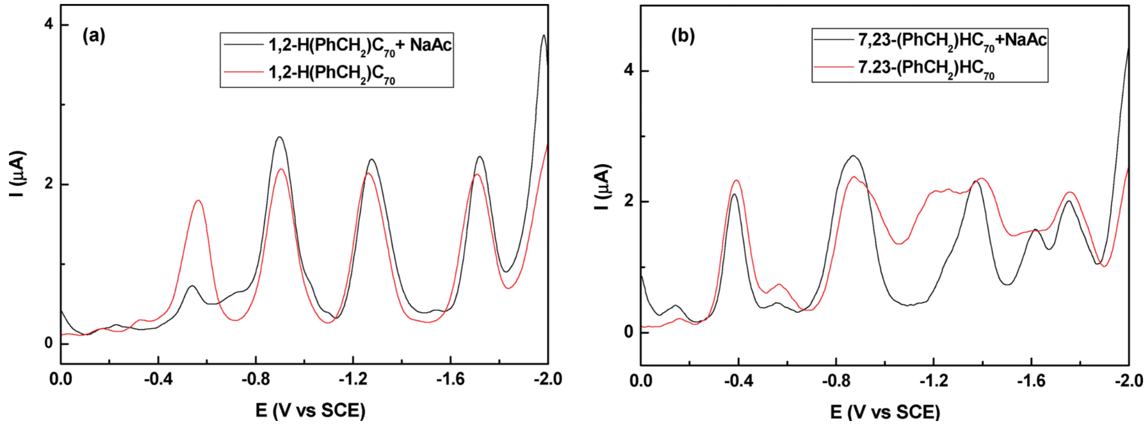


Fig. 5 DPV of (a) 1,2-H($PhCH_2$)C_{70} and (b) 7,23-($PhCH_2$)HC_{70} in *o*-DCB (*o*-dichlorobenzene) containing 0.1 M TBAP. Red line: without addition of NaAc; Black line: with the addition of 1.3 equivalent of NaAc dissolved in DMSO.

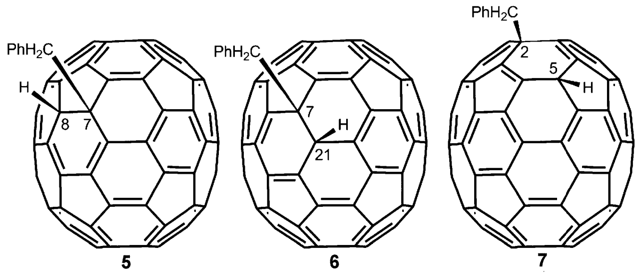
therefore demonstrate that 1,2-H(PhCH$_2$)C$_{70}$ is much more acidic than 7,23-(PhCH$_2$)HC$_{70}$, which may lead to different D$_2$O effect on the formation of the two regioisomers.

Theoretical and mechanistic considerations

Previous work has shown that C$_{60}^{2-}$ and C$_{70}^{2-}$ react with organic halides in a stepwise manner.[7b,8,10] The intermediates of RC$_{60}^{-}$ and RC$_{70}^{-}$ are produced during the first step *via* the radical couplings of C$_{2n}^{-\bullet}$ (n = 30 or 35) with R$^\bullet$, which are formed by single electron transfer from C$_{2n}^{2-}$ to the RX.[7b,8] RC$_{2n}^{-}$ can then be utilized to prepare RHC$_{2n}$ by quenching with suitable proton donors.[10,11b,29] It indicates that under the current experimental conditions, 2-PhCH$_2$C$_{70}^{-}$ and 7-PhCH$_2$C$_{70}^{-}$ intermediates should be favorably formed first before the protonation with water.

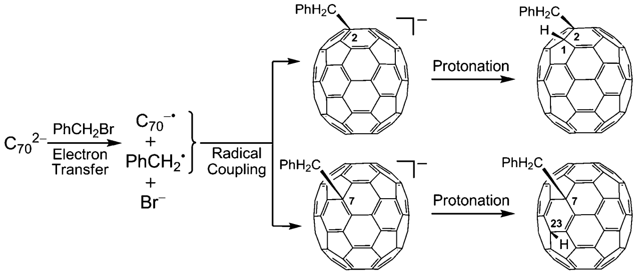
Density functional theory (DFT) calculations with the Gaussian 03 program[30] at the B3LYP/6-31G level[31] were carried out to rationalize the favorable formation of the 2-PhCH$_2$C$_{70}^{-}$ and 7-PhCH$_2$C$_{70}^{-}$ intermediates in the first step. The calculations predict that the energies are −2937.6019, −2937.6136, −2937.6069, −2937.6095 and −2937.5831 a.u. (1 a.u. = 627.5 kcal mol^{-1}) for the optimized structures of 1-PhCH$_2$C$_{70}^{-}$, 2-PhCH$_2$C$_{70}^{-}$, 5-PhCH$_2$C$_{70}^{-}$, 7-PhCH$_2$C$_{70}^{-}$ and 21-PhCH$_2$C$_{70}^{-}$ respectively, indicating that the 2-PhCH$_2$C$_{70}^{-}$ and 7-PhCH$_2$C$_{70}^{-}$ are the most stable intermediates, with an energy of 19.1 and 16.6 kcal mol^{-1} lower than that of the most unfavorable 21-PhCH$_2$C$_{70}^{-}$ intermediate.

The next question is why the subsequent protonation prefers to occur at the C23 for 7-PhCH$_2$C$_{70}^{-}$ and C1 for 2-PhCH$_2$C$_{70}^{-}$. Scheme 3 shows the other possible regioisomers (**5**–**7**) that might be formed from the protonation of 7-PhCH$_2$C$_{70}^{-}$ and 2-PhCH$_2$C$_{70}^{-}$ intermediates.



Scheme 3 Illustrated structures of possible (PhCH$_2$)HC$_{70}$ regioisomers from the *ortho*-addition of 7-PhCH$_2$C$_{70}^{-}$ and *para*-addition of 2-PhCH$_2$C$_{70}^{-}$.

For the 7-PhCH$_2$C$_{70}^{-}$ intermediate, two possible regioisomers **5** and **6** can be formed *via* the subsequent protonation at C8 and C21 with *ortho*-addition. Similarly, there is also possibility to form regioisomer **7** from 2-PhCH$_2$C$_{70}^{-}$ intermediate *via* the protonation at C5 with *para*-addition. In fact, C$_{70}$ derivatives with the configurations of **5** and **6** have been reported for the benzyne adducts,[22] while derivatives with peroxide addends have been shown to have the configuration of **7**.[13a] The calculated total energies for **2**, **5** and **6** are −2938.1227, −2938.1173, and −2938.1031 a.u. respectively, predicting that **5** and **6** are less stable by 3.4 and 12.3 kcal mol^{-1} with respect to 7,23-(PhCH$_2$)HC$_{70}$ (**2**, Scheme 2). For **4** and **7**, the calculated energies are −2938.1340 and −2938.1212 a.u. respectively, predicting that **7** is less stable than 1,2-H(PhCH$_2$)C$_{70}$ (**4**, Scheme 2) by 8.0 kcal/mol. The results indicate that the formation of the (PhCH$_2$)HC$_{70}$ regioisomers are thermodynamically controlled, and imply that the *ortho*-addition pattern is preferred for the addition in the polar region of C$_{70}$, similar to the addition preference of C$_{60}$. But for the addition in the equatorial region of C$_{70}$, a *para*-addition is more preferable over an *ortho*-addition due to the unique electronic structure of C$_{70}$. The reaction mechanism for the formation of 1,2-H(PhCH$_2$)C$_{70}$ and 7,23-(PhCH$_2$)HC$_{70}$ is proposed and illustrated in Scheme 4.



Scheme 4 Proposed reaction mechanism for the formation of 1,2-H(PhCH$_2$)C$_{70}$ and 7,23-(PhCH$_2$)HC$_{70}$ regioisomers.

Conclusion

A novel equatorial organo(hydro)[70]fullerene product with the appendages positioned in *para*-manner is obtained *via* the reaction of C$_{70}^{2-}$ with benzyl bromide and H$_2$O. The preferable formation of such a regioisomer is rationalized by theoretical calculations. ^{1}H NMR, D$_2$O experiment, and cyclic voltammetry have all demonstrated different properties between 7,23-(PhCH$_2$)HC$_{70}$ and 1,2-H(PhCH$_2$)C$_{70}$, indicating a significant structural difference between the equatorial and polar regions of C$_{70}$. More surprisingly, the equatorial regioisomer exhibits a positively shifted reduction potential with respect to those of the polar adduct and even the pristine C$_{70}$, suggesting that the equatorial region of C$_{70}$ is rather electropositive than electronegative.

Experimental

Chemicals and instrumentation

C$_{70}$ (99%) was purchased and used without further purification. Electrochemical grade TBAP was recrystallized from absolute ethanol and dried in vacuum at 298 K prior to use. Benzonitrile (PhCN, 99.9%) was purchased and distilled over P$_2$O$_5$ under vacuum at 305 K prior to use. All other chemicals were commercially available and used as received. The amount of water residue in freshly distilled PhCN and commercial available DMF is about 90 and 2000 ppm measured using the Karl Fischer titration method.

Controlled-potential bulk electrolysis was carried out with a potentiostat/galvanostat. NMR spectra were measured on a Bruker AV 600 instrument. HRMS experiments were performed on a FT-ICR MS equipped with a 7.0 T actively shielded superconducting magnet. MALDI MS was acquired on a Bruker Autofelx III TOF/TOF instrument. Uv-vis spectra were recorded on a PerkinElmer Lamda 900 UV-Vis-NIR spectrophotometer.

Synthesis of $H(PhCH_2)C_{70}$ regioisomers

Typically, 50 mg (59.5 μmol) of C_{70} was electrolyzed at −1.0 V *vs.* SCE in 50 mL of DMF solution containing 0.1 M TBAP under an argon atmosphere at about 15 °C. The potentiostat was switched off after the electrolytic formation of C_{70}^{2-} was complete, and a 30-fold excess of $PhCH_2Br$ was added to the solution under inert atmosphere. The reaction was allowed to proceed for about 4 h with stirring. The mixture was dried with a rotary evaporator under reduced pressure, and the residue was washed with methanol to remove TBAP and excessive $PhCH_2Br$. The obtained crude mixture was put into toluene and sonicated for 10 min, and the soluble part was further purified by HPLC over a semi-preparative Buckyprep column with toluene as the eluent. Isolated yields are about 5%, 10%, 5%, 25%, and 15% for **P1** (7,23-$(PhCH_2)_2C_{70}$), **P2** (7,23-$(PhCH_2)HC_{70}$), **P3** (mixture of 2,1- and 5,6-$H(PhCH_2)C_{70}$), **P4** (1,2-$H(PhCH_2)C_{70}$), and **P5** (unreacted C_{70}) respectively.

Synthesis of partially deuterated $H(PhCH_2)C_{70}$ regioisomers

The processes for the synthesis of deuterated regioisomers are similar to those mentioned above, except that 100 μL of D_2O was added into the freshly distilled DMF solvent (50 mL) before electrolysis.

Synthesis of $H(PhCH_2)C_{70}$ regioisomers in PhCN

The procedures for the synthesis of $H(PhCH_2)C_{70}$ regioisomers in PhCN solution are similar to those in DMF solution, except that 200 μL of H_2O was added into 50 mL of freshly distilled PhCN after the reaction between C_{70}^{2-} with 30-fold benzyl bromide underwent for 5 min.

Electrochemistry of 1,2-$H(PhCH_2)C_{70}$ and 7,23-$(PhCH_2)HC_{70}$

Measurements were performed in a 0.1 M TBAP benzonitrile solution with the use of a homemade cell equipped with a glassy carbon working electrode, platinum counter electrode and SCE (saturated calomel electrode) as a reference electrode. Scan rate was 0.1 V/s. The SCE was separated from the solution by a fritted-glass bridge of low porosity which contained the solvent/supporting electrolyte mixture.

Evaluation of the pK_as for 1,2-$H(PhCH_2)C_{70}$ and 7,23-$(PhCH_2)HC_{70}$ with DPV

About 1 mg of individual compound was dissolved in 2 mL *o*-DCB solution containing 0.1 M TBAP. The solution was purged with argon for 10 min prior to DPV measurement. Then 1.3 equivalent of sodium acetate, which was dissolved in DMSO, was added into the individual $H(PhCH_2)C_{70}$ regioisomer *o*-DCB solution, and the DPV was measured.

Spectral characterisation of 1,2-$H(PhCH_2)C_{70}$

The spectral data are consistent with previous results.[11b] Negative ESI FT-ICR MS: *m*/*z* $[M-H]^-$ calcd 931.05478, found 931.05324; ^1H NMR (600 MHz, $CS_2/CDCl_3$) δ 4.07 (s, 2H), 4.50 (s, 1H), 7.64 (d, 2H), 7.48 (t, 2H), 7.39 (t, 1H); ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) δ 158.15 (2C), 155.05 (2C), 151.05 (2C), 150.99 (4C), 150.87 (2C), 150.47 (2C), 150.40 (2C), 149.60 (2C), 149.41 (2C), 149.26 (2C), 149.17 (2C), 148.89 (2C), 148.67 (2C), 148.57 (2C), 147.23 (2C), 147.02 (2C), 146.85 (2C), 146.75 (1C), 146.43 (2C), 146.08 (2C), 145.61 (2C), 145.34 (3C), 142.87 (2C), 142.65 (2C), 142.58 (2C), 142.26 (2C), 140.51 (2C), 140.03 (2C), 137.72 (2C), 133.64 (2C), 133.58 (2C), 130.89 (2C), 130.78 (2C), 135.11 (1C, Ph), 130.89 (2C, Ph), 128.62 (2C, Ph), 127.56 (1C, Ph), 57.3 (1C, sp^3, C–CH_2), 52.4 (1C, sp^3, C–H), 51.5 (1C, sp^3, CH_2).

Spectral characterisation of 7,23-$(PhCH_2)HC_{70}$

Negative ESI FT-ICR MS: *m*/*z* $[M-H]^-$ calcd 931.05478, found 931.05629; ^1H NMR (600 MHz, CS_2/acetone-d_6) δ 6.68–6.50 (m, 5H), 2.96 (ABq, $\Delta\nu_{AB} = 94$ Hz, $J_{AB} = 12.6$ Hz, 2H), 2.79 (s, 1H); ^1H NMR (600 MHz, $CS_2/CDCl_3$) δ 7.27–7.05 (m, 5H), 3.55 (ABq, $\Delta\nu_{AB} = 92$ Hz, $J_{AB} = 12.6$ Hz, 2H), 3.40 (s, 1H); ^1H NMR (600 MHz, CS_2/DMSO-d_6) δ 7.00–6.81 (m, 5H), 3.27 (ABq, $\Delta\nu_{AB} = 93$ Hz, $J_{AB} = 13.2$ Hz, 2H), 3.10 (s, 1H); ^{13}C NMR (150 MHz, CS_2/DMSO-d_6) δ 157.41 (1C), 154.18 (1C), 150.97 (1C), 150.13 (1C), 149.88 (1C), 149.47 (1C), 149.15 (1C), 149.08 (1C), 148.99 (1C), 148.97 (1C), 148.56 (1C), 148.52 (1C), 148.14 (1C), 148.07 (1C), 147.99 (1C), 147.91 (1C), 147.87 (1C), 147.67 (1C), 147.52 (1C), 147.45 (1C), 146.74 (1C), 146.69 (1C), 146.60 (1C), 146.56 (1C), 146.43 (1C), 146.36 (2C), 146.18 (1C), 146.08 (1C), 145.30 (2C), 145.25 (1C), 145.21 (1C), 144.89 (1C), 144.71 (1C), 144.58 (1C), 144.55 (1C), 144.44 (2C), 144.16 (1C), 143.93 (1C), 143.88 (1C), 143.66 (2C), 143.47 (1C), 143.45 (1C), 143.28 (1C), 142.50 (1C), 142.35 (2C), 142.19 (1C), 141.60 (1C), 141.55 (1C), 141.31 (1C), 140.57 (1C), 140.54 (1C), 138.77 (1C), 138.42 (1C), 136.41 (1C), 135.04 (1C, Ph), 134.56 (1C), 133.45 (1C), 133.41 (1C), 133.36 (1C), 133.25 (1C), 132.88 (1C), 132.80 (1C), 131.40 (1C), 131.24 (1C), 130.20 (2C, Ph), 127.60 (2C, Ph), 126.62 (1C, Ph), 56.88 (1C, sp^3, C–CH_2), 46.46 (1C, sp^3, CH_2), 44.66 (1C, sp^3, C–H).

Spectral characterisation of 7,23-$(PhCH_2)_2C_{70}$

The spectral data are consistent with previous results.[11a] Positive MALDI MS: *m*/*z* $[M+H]^+$ calcd 1023.1, found 1023.1; ^1H NMR (600 MHz, $CS_2/CDCl_3$) δ 7.27–7.20 (m, 10H), 3.62 (ABq, $\Delta\nu_{AB} = 22$ Hz, $J_{AB} = 13.2$ Hz, 4H); ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) δ 157.90 (2C), 150.68 (2C), 150.22 (2C), 150.15 (2C), 149.38 (2C), 148.49 (2C), 148.41 (2C), 148.28 (2C), 148.06 (2C), 147.96 (2C), 147.05 (2C), 146.94 (2C), 146.73 (2C), 146.66 (2C), 146.53 (2C), 145.77 (2C), 145.56 (2C), 145.02 (2C), 144.92 (2C), 144.85 (2C), 144.49 (2C), 144.19 (2C), 143.98 (2C), 143.31 (2C), 142.53 (2C), 142.15 (2C), 141.75 (2C), 140.81 (2C), 139.70 (2C), 139.01 (2C), 135.26 (1C, Ph), 133.80 (2C), 133.74 (2C), 133.27 (2C), 131.75 (2C), 130.24 (2C, Ph), 128.05 (2C, Ph), 127.28 (1C, Ph), 57.04 (2C, C–CH_2), 49.61 (2C, CH_2).

Quantum computational methods

The Gaussian full geometry optimizations of 1-$PhCH_2C_{70}^-$, 2-$PhCH_2C_{70}^-$, 5-$PhCH_2C_{70}^-$, 7-$PhCH_2C_{70}^-$, 21-$PhCH_2C_{70}^-$ intermediates and **2**, **4**, **5**, **6**, **7** were performed by using the B3LYP functional and 6-31G basis set in the Gaussian 03 program package, followed by harmonic frequency calculations at the same level to confirm them as the energy minima.

Acknowledgements

The work was supported by the National Natural Science Foundation of China (Grant No. 20972150), and the Solar Energy Initiative of the Chinese Academy of Sciences (Grant No. KGCX2-YW-399 + 9).

Notes and references

1 W. Krätschmer, L. D. Lamb, K. Fostiropoulos and D. R. Huffman, *Nature*, 1990, **347**, 354–358.

2 (*a*) P. M. Allemand, A. Koch, F. Wudl, Y. Rubin, F. Diederich, M. M. Alvarez, S. J. Anz and R. L. Whetten, *J. Am. Chem. Soc.*, 1991, **113**, 1050–1051; (*b*) Q. Xie, E. Perez-Cordero and L. Echegoyen, *J. Am. Chem. Soc.*, 1992, **114**, 3978–3980.

3 (*a*) A. Hirsch and M. Brettreich, *Fullerene: Chemistry and Reactions*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2005; (*b*) P. A. Troshin and R. N. Lyubovskaya, *Russ. Chem. Rev.*, 2008, **77**, 305–349; (*c*) C. Thilgen, A. Herrmann and F. Diederich, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2268–2280.

4 (*a*) C. C. Henderson, C. M. Rohifing, K. T. Gillen and P. A. Cahill, *Science*, 1994, **264**, 397–399; (*b*) C. Thilgen and F. Diederich, *Top. Curr. Chem.*, 1999, **199**, 135–171.

5 E. W. Godly and R. Taylor, *Pure Appl. Chem.*, 1997, **69**, 1411–1434.

6 (*a*) M. M. Wienk, J. M. Kroon, W. J. H. Verhees, J. Knol, J. C. Hummelen, P. A. van Hal and R. A. J. Janssen, *Angew. Chem., Int. Ed.*, 2003, **42**, 3371–3375; (*b*) J. Y. Kim, K. Lee, N. E. Coates, D. Moses, T. Q. Nguyen, M. Dante and A. J. Heeger, *Science*, 2007, **317**, 222–225.

7 (*a*) C. Caron, R. Subramanian, F. D'Souza, J. Kim, W. Kunter, M. T. Jones and K. M. Kadish, *J. Am. Chem. Soc.*, 1993, **115**, 8505–8506; (*b*) K. M. Kadish, X. Gao, O. Gorelik, E. Van Caemelbecke, T. Suenobu and S. Fukuzumi, *J. Phys. Chem. A*, 2000, **104**, 2902–2907.

8 (*a*) R. Subramanian, K. M. Kadish, M. N. Vijayashree, X. Gao, M. T. Jones, D. M. Miller, K. Krause, T. Suenobu and S. Fukuzumi, *J. Phys. Chem.*, 1996, **100**, 16327–16335; (*b*) S. Fukuzumi, T. Suenobu, T. Hirasaka, R. Arakawa and K. M. Kadish, *J. Am. Chem. Soc.*, 1998, **120**, 9220–9227.

9 (*a*) H. P. Spielmann, G. W. Wang, M. S. Meier and B. R. Weedon, *J. Org. Chem.*, 1998, **63**, 9865–9871; (*b*) Z. Wang and M. S. Meier, *J. Org. Chem.*, 2003, **68**, 3043–3048.

10 W.-W. Yang, Z.-J. Li and X. Gao, *J. Org. Chem.*, 2010, **75**, 4086–4094.

11 (*a*) M. S. Meier, R. G. Bergosh, M. E. Gallagher, H. P. Spielmann and Z. Wang, *J. Org. Chem.*, 2002, **67**, 5946–5952; (*b*) Z. Wang and M. S. Meier, *J. Org. Chem.*, 2004, **69**, 2178–2180.

12 W.-W. Yang, Z.-J. Li and X. Gao, *J. Org. Chem.*, 2011, **76**, 6067–6074.

13 (*a*) Z. Xiao, F. Wang, S. Huang, L. Gan, J. Zhou, G. Yuan, M. Lu and J. Pan, *J. Org. Chem.*, 2005, **70**, 2060–2066; (*b*) T. Kitagawa, Y. Lee, N. Masaoka and K. Komatsu, *Angew. Chem., Int. Ed.*, 2005, **44**, 1398–1401; (*c*) A. D. Darwish, A. G. Avent, R. Taylor and D. R. M. Walton, *J. Chem. Soc., Perkin Trans. 2*, 1996, 2079–2084.

14 P. J. Fagan, P. J. Krusic, D. H. Evans, S. A. Lerke and E. Johnston, *J. Am. Chem. Soc.*, 1992, **114**, 9697–9699.

15 G. P. Miller and M. C. Tetreau, *Org. Lett.*, 2000, **2**, 3091–3094.

16 (*a*) A. B. Smith, R. M. Strongin, L. Brard, G. T. Furst, W. J. Romanow, K. G. Owens, R. J. Goldschmidt and R. C. King, *J. Am. Chem. Soc.*, 1995, **117**, 5492–5502; (*b*) M. S. Meier and J. Kiegiel, *Org. Lett.*, 2001, **3**, 1717–1719; (*c*) P. A. Troshin, A. S. Peregudov, S. M. Peregudova and R. N. Lyubovskaya, *Eur. J. Org. Chem.*, 2007, **35**, 5861–5866; (*d*) G.-W. Wang, H.-T. Yang, P. Wu and C.-Z. Wang, *Eur. J. Org. Chem.*, 2010, 5714–5721.

17 M. Zheng, F.-F. Li, Z. Shi, X. Gao and K. M. Kadish, *J. Org. Chem.*, 2007, **72**, 2538–2542.

18 R. M. Silverstein and F. X. Webster, *Spectrometric Identification of Organic Compounds*, 6th ed., John Wiley & Sons, Inc., New York, 1998, p. 263.

19 (*a*) F.-F. Li, W.-W. Yang, G.-B. He and X. Gao, *J. Org. Chem.*, 2009, **74**, 8071–8077; (*b*) W.-W. Yang, Z.-J. Li, F.-F. Li and X. Gao, *J. Org. Chem.*, 2011, **76**, 1384–1389.

20 (*a*) M. S. Meier, H. P. Spielmann, R. G. Bergosh and R. C. Haddon, *J. Am. Chem. Soc.*, 2002, **124**, 8090–8094; (*b*) M. S. Meier, H. P. Spielmann, R. G. Bergosh and M. C. Tetreau, *J. Org. Chem.*, 2003, **68**, 7867–7870.

21 (*a*) M. Prato, T. Suzuki, F. Wudl, V. Lucchini and M. Maggini, *J. Am. Chem. Soc.*, 1993, **115**, 7876–7877; (*b*) T. Sternfeld, R. E. Hoffman, C. Thilgen, F. Diederich and M. Rabinovitz, *J. Am. Chem. Soc.*, 2000, **122**, 9038–9039; (*c*) M. Bühl and A. Hirsch, *Chem. Rev.*, 2001, **101**, 1153–1183; (*d*) T. Sternfeld, C. Thilgen, R. E. Hoffman, M. R. C. Heras, F. Diederich, F. Wudl, L. T. Scott, J. Mack and M. Rabinovitz, *J. Am. Chem. Soc.*, 2002, **124**, 5734–5738; (*e*) Z. Chen and R. B. King, *Chem. Rev.*, 2005, **105**, 3613–3642.

22 M. S. Meier, G.-W. Wang, R. C. Haddon, C. P. Brock, M. A. Lloyd and J. P. Selegue, *J. Am. Chem. Soc.*, 1998, **120**, 2337–2342.

23 B. Li, C. Shu, X. Lu, L. Dunsch, Z. Chen, T. J. S. Dennis, Z. Shi, L. Jiang, T. Wang, W. Xu and C. Wang, *Angew. Chem. Int. Ed.*, 2010, **49**, 962–966.

24 (*a*) M. Carano, T. Da Ros, M. Fanti, K. Kordatos, M. Marcaccio, F. Paolucci, M. Prato, S. Roffia and F. Zerbetto, *J. Am. Chem. Soc.*, 2003, **125**, 7139–7144; (*b*) A. A. Popov, I. E. Kareev, N. B. Shustova, E. B. Stukalin, S. F. Lebedkin, K. Seppelt, S. H. Strauss, O. V. Boltalina and L. Dunsch, *J. Am. Chem. Soc.*, 2007, **129**, 11551–11568.

25 T. F. Guarr, M. S. Meier, V. K. Vance and M. Clayton, *J. Am. Chem. Soc.*, 1993, **115**, 9862–9863.

26 L. Echegoyen and L. E. Echegoyen, *Acc. Chem. Res.*, 1998, **31**, 593–601.

27 (*a*) M. D. Tzirakis and M. Orfanopoulos, *Org. Lett.*, 2008, **10**, 873–876; (*b*) M. D. Tzirakis, M. N. Alberti and M. Orfanopoulos, *Chem. Commun.*, 2010, **46**, 8228–8230; (*c*) M. F. Tzirakis and M. Orfanopoulos, *J. Am. Chem. Soc.*, 2009, **131**, 4063–4069.

28 (*a*) M. E. Niyazymbetov, D. H. Evans, S. A. Lerke, P. A. Cahill and C. C. Henderson, *J. Phys. Chem.*, 1994, **98**, 13093–13098; (*b*) B. Jousselme, G. Sonmez and F. Wudl, *J. Mater. Chem.*, 2006, **16**, 3478–3482.

29 (*a*) A. Hirsch, A. Soi and H. R. Karfunkel, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 766–768; (*b*) H. Nagashima, H. Terasaki, E. Kimura, K. Nakajima and K. Itoh, *J. Org. Chem.*, 1994, **59**, 1246–1248; (*c*) K. Komatsu, Y. Murata, N. Takimoto, S. Mori, N. Sugita and T. S. M. Wan, *J. Org. Chem.*, 1994, **59**, 6101–6102; (*d*) E. Allard, F. Cheng, S. Chopin, J. Delaunay, D. Rondeau and J. Cousseau, *New J. Chem.*, 2003, **27**, 188–192; (*e*) E. Champeil, C. Crean, C. Larraya, G. Pescitelli, G. Proni and L. Ghosez, *Tetrahedron*, 2008, **64**, 10319–10330.

30 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Jr. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03, Revision D.01*, Gaussian, Inc., Wallingford, CT, 2004.

31 (*a*) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652; (*b*) C. T. Lee, W. T. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785–789.