Exohedrally stabilized C$_{70}$ isomer with adjacent pentagons characterized by crystallography†

Yuan-Zhi Tan, Jia Li, Ming-Yue Du, Shui-Chao Lin, Su-Yuan Xie,* Xin Lu,* Rong-Bin Huang and Lan-Sun Zheng

All C$_{70}$ isomers other than the well-known $D_{5h}$-symmetric C$_{70}$ (#8149) are highly elusive due to their defiance of the isolated pentagon rule (IPR), and, in turn, have long been underrated for years. Here we show a non-IPR hollow C$_{70}$ (#8064) with $C_2$-symmetry stabilized by exohedral chlorination as #8064C$_{70}$Cl$_{10}$. Its connectivity with two pairs of fused pentagons was determined unambiguously by single crystal X-ray diffraction analysis. Based on the geometric criterion in terms of the pyramidalization angle as well as theoretical computations on the Kekulé structure and the negative nucleus independent chemical shift, the exohedral stabilization of the labile #8064C$_{70}$ is rationalized by releasing the local strain relevant to the fused pentagons and achieving the aromaticity of the remaining sp$^2$-hybridized carbon framework in the exohedral derivative of #8064C$_{70}$. This new entrant in the C$_{70}$ family, in addition to two previously reported non-IPR isomers (by Yang, Dunsch et al. for Sc$_3$N@#7854C$_{70}$ and by Echegoyen et al. for Sc$_2$S@#7892C$_{70}$), provides valuable opportunities for experimental and theoretical research involving non-IPR isomers of C$_{70}$ beyond the common $D_{5h}$-C$_{70}$.

Results and discussion

Soot containing fullerenes was synthesized in a modified Krätschmer–Huffman arc-discharge reactor under an atmosphere of helium and CCl$_4$. Extracted using toluene in a supersonic bath, the toluene-soluble components were separated by five stages of HPLC isolation. About 2 mg of the purified C$_{70}$Cl$_{10}$ was obtained for further identification [the detailed separation procedure is described in the ESI†].

The purified sample was analyzed using an analytical Buckyprep column. As shown in Fig. 1a, the predominant peak at the retention time of $\sim$20.2 min indicates the high purity of the as-purified compound. In the corresponding mass spectrum (Fig. 1b), good agreement of the experimental isotopic pattern of 1 with the simulated one (inset in Fig. 1b) validates the proposed composition of C$_{70}$Cl$_{10}$. The bare cage of C$_{70}$ (840 m/z) deriving from dechlorination was hardly detected by single-stage mass spectrometry with an atmospheric pressure chemical ionization (APCI) source. Only a minor peak corresponding to a C$_{70}$Cl$_8$ fragment was recorded even at a furnace temperature of up to 350 °C (Fig. 1b). By contrast, APCI-mass spectra of...
IPR-satisfying $D_{5h}^{#8149}C_{70}$ chlorides typically contain obvious mass peaks assignable to the pristine fullerene cage of $C_{70}$.\textsuperscript{10–12} The different profiles in the mass spectrometric analyses indicate the thermal stability of 1 superior to the IPR-satisfying chlorofullerenes of $D_{5h}^{#8149}C_{70}$, as supported by the geometric and theoretical analyses (vide infra).

$^{#8064}C_{70}Cl_{10}$ is soluble in common organic solvents, such as toluene, chloroform and carbon disulfide. Its UV/Vis spectrum in toluene shows a broad absorption in the solar spectrum region with visible peaks at 440, 517 and 555 nm. The optical absorption onset of 1 is at ~600 nm, comparable to the broad absorption of $D_{5h}^{#8149}C_{70}$ decachloride ($^{#8149}C_{70}Cl_{10}$),\textsuperscript{14} with implications for the non-IPR isomer of $C_{70}$ holding attractive potentialities similar to its cousin $D_{5h}^{#8149}C_{70}$ for promising photovoltaic applications.\textsuperscript{2,3}

A single crystal grown from chloroform solution was selected to identify the geometric structure of 1 by X-ray diffraction. The crystallographic data\textsuperscript{4} reveal two pairs of fused pentagons on the chiral cage of $C_{2}$-symmetric $^{#8064}C_{70}$ (Fig. 2a). The carbon atoms at the pentagon fusions are bonded to four chlorine atoms separately, and the additional six 1,4 positions in the three hexagons are bonded to the remaining six chlorine atoms (Fig. 2a). X-Ray crystallographic data also disclose interesting crystal packing which is relevant to the assembly and charge transport of 1 in the solid state. Three kinds of weak intermolecular interactions (i.e., C–Cl⋯C–Cl, C–Cl⋯π and π⋯π interactions) account for the packing of $^{#8064}C_{70}Cl_{10}$ molecules in the crystal (Fig. 2b). Of interest is the pattern of fullerene molecules in the [101] facets, which is similar to the honeycomb net of graphene (Fig. 2c). Each cavity of this hcb-6\textsuperscript{3} net is filled by two co-crystallized chloroform molecules, linking to the surrounding $^{#8064}C_{70}Cl_{10}$ molecules through C–Cl⋯π interactions.

In contrast to the non-IPR $C_{70}$ isomers already-stabilized by encapsulation of endo-clusters (Sc$_3$N or Sc$_2$S),\textsuperscript{8,9} the exohedral groups of 1 are ready to be removed and sequentially to form a pristine non-IPR $C_{70}$ cage. By stepwise dechlorination through colliding with helium gas in the ion trap of the mass spectrometer, the formation of pristine $^{#8064}C_{70}$ can be observed (Fig. 3). Multistage mass spectrometry (MS$^n$, $n$ = 1–5) shows the formation of pristine $^{#8064}C_{70}$ by progressive dechlorination from $^{#8064}C_{70}Cl_{10}$ ($m$ = 1–10) ($m$ value is indicated as the number in blue on the bottom line, and the species selected for the next stage of the fragmentation are marked with colored asterisks).
spectra, as shown in Fig. 3, pristine non-IPR \( C_2 \#^{8064}C_{70} \) can be produced from 1 in the gas phase.

To compare the stability of pristine or chlorinated \( C_{70} \) isomers, theoretical computations on IPR-satisfying and non-IPR \( C_{70} \) species were performed at the GGA-PBE/DNP level of theory.\(^{13,14} \) As expected, \( C_2 \#^{8064}C_{70} \) is less stable than \( D_{5h} \#^{8149}C_{70} \) and is too labile to survive in the ambient conditions. The energy of pristine \( C_2 \#^{8064}C_{70} \) is 48.8 kcal mol\(^{-1} \) higher than that of \( D_{5h} \#^{8149}C_{70} \), and the HOMO–LUMO gap of non-IPR \( \#^{8064}C_{70} \) (0.65 eV) is smaller than that of the IPR one (1.72 eV for \( D_{5h} \#^{8149}C_{70} \)). By chlorination, however, the energy of 1 is 10.6 kcal mol\(^{-1} \) lower than that of \( \#^{8149}C_{70}Cl_{10} \). The band gap of 1 increases to 2.07 eV, close to that of \( \#^{8149}C_{70}Cl_{10} \) (2.10 eV).\(^{18} \) Therefore, in agreement with the mass spectra discussed above, the stability of 1 is higher than the previously synthesized IPR-satisfying \( \#^{8149}C_{70}Cl_{10} \).\(^{18} \) This is also analogous to the cases of previously reported non-IPR chlorofullerenes \( \#^{18917}C_{70}Cl_{24} \) (ref. 15) or \( \#^{1809}C_{60}Cl_8 \) (ref. 16) with lower energies relative to their corresponding IPR-satisfying cousins. Accordingly, it is not surprising that pristine non-IPR \( \#^{8064}C_{70} \) is highly elusive but can be captured in the solid state. These theoretical data also lend credence to the expectation that numerous isomers of \( C_{70} \) with adjacent pentagons might be synthesized and identified in the near future.

With respect to geometric criteria, the local strain of a fullerene molecule can be probed in terms of the pyramidalization angle \( \theta_p \).\(^{17} \) A higher value of \( \theta_p \) indicates a higher strain of the \( sp^3 \)-hybridized carbon involved and sequentially facilitates the \( sp^3 \)-to-\( sp^3 \) hybridization conversion. For the pristine \( \#^{8064}C_{70} \), the \( \theta_p \) values of carbon atoms at the pentagon fusions are 16.0 and 14.6° whereas the other sites have much smaller \( \theta_p \) values with an average of 10.4° (see the ESI for the coordinates of the computationally optimized \( \#^{8064}C_{70} \) in detail).\(^{31} \) At the pentagon fusions, therefore, \( \#^{8064}C_{70} \) is ready to bond with foreign groups to transfer their hybridization state from \( sp^3 \) to \( sp^3 \). In addition, the computational electronic structure of pristine \( \#^{8064}C_{70} \) shows that larger coefficients of the HOMO and LUMO functions locate at the pentagon fusions, which supports the preferential occurrence of the addition reaction at these sites (see the ESI, Fig. S2†). Indeed, in 1 all the pentagon fusion sites are bonded with chlorine atoms to decrease the \( \theta_p \) values from \( \sim 16.0-14.6^\circ \) to \( \sim 4.0-2.7^\circ \) (note that the \( \theta_p \) for an \( sp^3 \)-hybridized carbon is defined in ref. 18). The strain relief is therefore fulfilled in 1, similar to the other non-IPR fullerenes stabilized by exohedral derivatization.\(^{15,16,18-28} \)

The ten \( sp^3 \)-hybridized carbon atoms in 1 form a ribbon to split the carbon cage of \( \#^{8064}C_{70} \) into two \( sp^3 \)-hybridized \( C_{30} \) fragments that are connected by a single C–C bond with a bond length of 1.50 Å (Fig. 4). Based on the criterion of a Kekulé structure, each \( C_{30} \) domain contains 38 Kekulé structures.\(^{29} \) This amount is comparable with those of three previously synthesized polycyclic aromatic hydrocarbon \( C_{28}H_{12} \) isomers with 35, 44 and 40 Kekulé structures, respectively (see the ESI, Fig. S3†), suggesting the aromaticity of the resultant \( sp^3 \)-hybridized carbon fragment in 1. Among them, 2 Kekulé structures of the \( C_{30} \) aromatic fragments are such that no double bonds are located at pentagons, satisfying the so-called Taylor criterion.\(^{32} \) In fact, the crystal data show that all the pentagons of the \( sp^3 \)-hybridized fragments are composed of single bonds with mean bond lengths of 1.45 Å, whereas the hexagons consist of alternating C=C/C=C bonds ranging from 1.36 to 1.49 Å or approximately equalized bonds ranging from 1.39 to 1.42 Å. Moreover, the aromaticity of the \( C_{30} \) fragments is also supported by remarkable negative nucleus independent chemical shift (NICS)\(^{33} \) values at the centers of rings (see the ESI, Fig. S4 and Table S1†). The local aromaticity in both \( C_{30} \) fragments brings additional stability for 1.\(^{28} \)

Topologically, the \( C_2 \#^{8064}C_{70} \) cage can be transformed to \( D_{5h} \#^{8149}C_{70} \) by two steps of a Stone–Wales (S–W) transformation through a heptagon-incorporating intermediate (Fig. 5). It has been long suspected that fullerene formation may undergo S–W transition.\(^{34} \) However, the activation barrier for S–W transformation was calculated to be as high as 7–8 eV.\(^{34} \) Such high barriers imply any S–W transition is hard to fulfill even in temperatures up to a thousand centigrade. In the presence of chlorine, however, conversion of a \( C_{76} \) cage from IPR to non-IPR was demonstrated to be viable at a temperature as low as 340 °C.\(^{35} \) For the present case, the co-existence of the topologically transformable IPR and non-IPR isomers of \( C_{70} \) in the chlorine-involved carbon arc-discharge conditions provides a valuable clue to further studies of the S–W mechanism involving \( C_{70} \). However, the possibility and mechanism of such a transformation remains to be detailed in the future.
Conclusions

As a hollow non-IPR member of the C70 family, the geometric structure, with two pairs of fused pentagons in an inherent chiral C2-symmetric cage, was unambiguously characterized by X-ray crystallography. Computational and geometrical analyses disclose the stabilization effects of C70 chloride, new insight into the C70 formation mechanism, as well as potentially useful properties of non-IPR C70 species with broad absorption. Starting from this work, we expected that further investigations of macroscopic synthesis, the formation mechanism and promising applications of C70 isomers with adjacent pentagon configurations might be stimulated.

Acknowledgements

This work was supported by the NSFC (grant numbers 21031004, U1205111, 21021061). We thank Professor Yu-Qi Feng from Wuhan University for HPLC support.

Notes and references

‡ Crystal of C70Cl10: 0.15 × 0.12 × 0.02 mm; triclinic; space group P1; a = 11.049(3), b = 13.430(4), c = 18.364(5) Å; α = 105.567(4), β = 91.091(4), γ = 106.254(4); V = 2507.1(11) Å³; Z = 2; T = 173(2) K; no. reflections = 17 260; no. independent reflections = 8182; full-matrix least-squares refinement on F²; final R indices (R₁ = 0.0867 and wR₂ = 0.2162 [R₁(all data) = 0.1057 and wR₂(all data) = 0.2342]).


