



**Significance:** An unprecedented, large molecular carbon, having a polycyclic aromatic surface composed of 85 fused hexagon rings, is synthesized. The nonplanar skeleton hampers compact  $\pi$ - $\pi$  stacking and bestows good solubility, thus allowing comprehensive structural characterizations.

**Comment:** The nonplanar polycyclic framework is found to undergo thermal isomerization, which renders a highly symmetrical isomer to be isolated. Single-crystal XRD analysis unambiguously proves the molecular structure.