

Synthesis and X-ray crystal structure of 1,3,5-tris(flouren-9-ylidenemethyl)benzene: towards a C₄₈-fragment of [60]-fullerene

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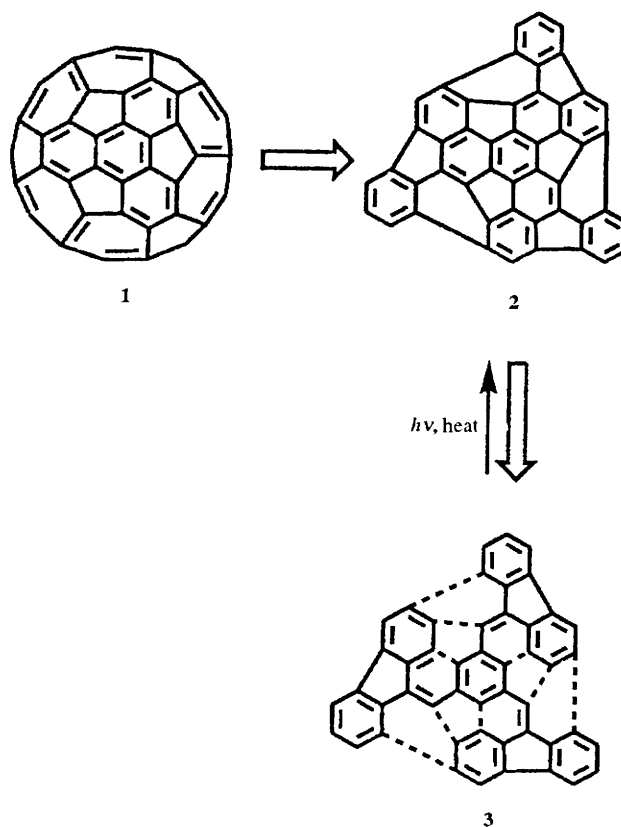
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Three-fold, stereoselective Wittig reactions between benzene-1,3,5-tricarbaldehyde **4** and fluoren-9-ylidene(triphenyl)phosphine **5** furnished an interesting C₄₈-hydrocarbon of C₃ symmetry whose crystal structure has been determined.

While there is burgeoning world-wide interest¹ in exploring the diverse chemistry of [60]-fullerene **1**, its preparation from graphite in one 'black box' operation is not only an embarrassment to practising synthetic chemists but also constitutes a serious challenge to them to create this molecule through rational, *de novo*, synthetic design. In synthetic efforts along 'classical' lines towards **1**, initiated in several laboratories,² C₂₀-corannulene,^{2b-d} C₂₁-sumanene^{2f,g} and C₃₀-hemicubminsterfullerene (5,5-circulene)^{2k,l} have received particular attention. Looking further ahead along the buckminsterfullerene surface, a C₄₈H₁₂ hydrocarbon **2** (C₆₀ - C₁₂ + H₁₂, 19 rings), a deep bowl of C₃-symmetry appeared to us an attractive proposition. We have envisioned an exceptionally short route to **2** via **3** through retrosynthetic protocols depicted below, in which its 48 carbons are sought to be assembled in one step from commercially available starting materials like fluorene (3 × C₁₃ = C₃₉) and mesitylene (C₉) through pre-installed complementary functionalities.

In practice, three-fold stereoselective Wittig reactions between benzene-1,3,5-tricarbaldehyde **4**³ and fluoren-9-ylidene(triphenyl)phosphine **5**⁴ through simple heating in chloroform turned out to be a very convenient way of obtaining the crystalline hydrocarbon **3** in one step and in 30% yield. The characteristic ¹H NMR resonance and the 16-line ¹³C NMR spectrum of **3** revealed both its structure as well as its C₃ symmetry. Elated at this ready access to **3**, we immediately attempted its three-fold photocyclization to **6** *en route* to **2**. We expected some difficulties in the photocyclization step on account of the non-coplanarity between the fluorenyl sheets and the central benzene ring but did not consider them to be insurmountable. However, despite many trials and a variety of reaction conditions (temperature, solvent, lamp, *etc.*), oxidative cyclization (in the presence of iodine, oxygen, *etc.*) of **3** → **6** could not be achieved.

A crystal structure determination of **3** was, therefore, undertaken and was found to be quite interesting on several counts. A perspective is shown in Fig. 1. The molecule **3** turned out to be 'propeller shaped' with the dihedral angle between the central benzene ring and the three fluorenylidene moieties being 40.0(2)°, 72.3(2)° and 106.3(2)°. The bond lengths and the bond angles are generally within the expected ranges. There is no evidence of twisting or folding at fluorenylidene double bonds. The angle between the orthogonally positioned fluorene moieties is 81°. There are several contacts ≈ 3 Å between aromatic carbons and the hydrogen atoms of the orthogonally positioned and partly off-set fluorenylidene sheets. The crystal structure of **3**, therefore appears to be predominantly stabilized through -CH...π interactions between the fluorenylidene moieties in a T-shape geometry. In the *xy* plane, the

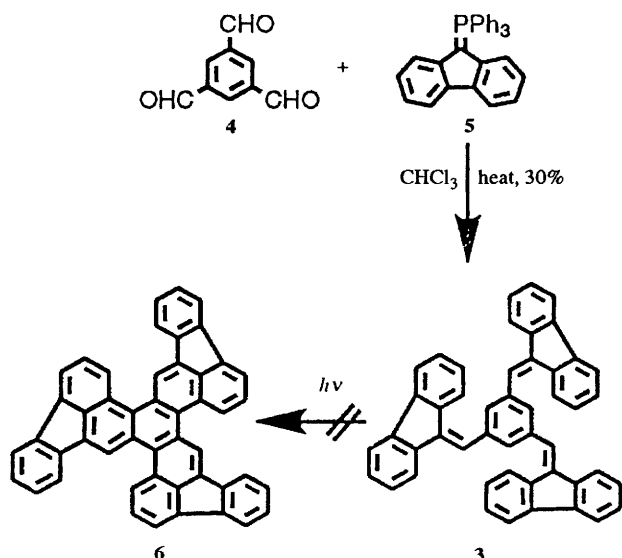


fluorenylidene moieties are off-set with respect to each other and despite the presence of many aromatic rings in the molecule there is hardly any face-to-face π-π stacking. An enclosed feature is also present between a pair of T-shaped fluorenylidene moieties and offers possibilities for co-crystallization with suitable aromatic guests.

Experimental

1,3,5-Tris(flouren-9-ylidenemethyl)benzene **3**

To a suspension of fluoren-9-ylidene(triphenyl)phosphine **5** (4.338 g, 10.18 mmol) in chloroform (100 cm³) was added benzene-1,3,5-tricarbaldehyde **4** (500 mg, 3.08 mmol) in chloroform. The contents of the flask were heated under reflux for 4 h after which chloroform was removed under reduced pressure. The residue was charged onto a silica gel column and elution with 5% ethyl acetate-hexane afforded **3** (575 mg, 30%)



as a solid residue. Recrystallization from chloroform-hexane gave fine crystals, mp 246–248 °C (Found: C, 95.0; H, 4.95. Calc. for $C_{48}H_{30}$: C, 95.02; H, 4.98); δ_H (200 MHz, $CDCl_3$) 7.85–7.65 (m, 6 H), 7.45–7.25 (m, 3 H) and 7.05–6.95 (m, 1 H); δ_C (50 MHz, $CDCl_3$), 141.5, 139.4, 138.1, 137.6, 136.6, 129.3, 128.8, 128.6, 128.4, 127.2, 126.9, 126.0, 124.6, 120.5, 119.9 and 119.7.

Crystal data

$C_{48}H_{30}$, colourless crystal, monoclinic, space group $P2_1/c$, $a = 13.377(2)$, $b = 21.595(4)$, $c = 12.337(2)$ Å units, $\beta = 111.78(2)^\circ$, $V = 3309(1)$ Å³, $Z = 4$, $D_c = 1.218$ g cm⁻³, $T = 293$ K, crystal dimensions 0.12 × 0.20 × 0.17 mm³. 4745 Reflections measured, range ($3 \leq 2\theta \leq 45$) and $0 \leq h \leq 16$, $0 \leq k \leq 25$, $-16 \leq l \leq 16$; 4353 unique reflections ($R_{int} = 0.028$), and 1221 observed with $I \geq 3\sigma(I)$, $\mu = 0.64$ cm⁻¹. Final $R = 0.053$ and $R_w = 0.059$ ($w = 1/\sigma^2(F_o) + 0.0002|F_o|^2$, goodness-of-fit = 1.08); maximum shift/error = 0.001, $\Delta\rho_{max} = 0.21$ e Å⁻³, $\Delta\rho_{min} = -0.17$ e Å⁻³. X-Ray experimental procedure: Mo-K α radiation ($\lambda = 0.71073$ Å), graphite crystal monochromator, Siemens R3m/v diffractometer (ω - 2θ scan technique). Data corrected for Lorentz and polarization correction but not for absorption. The structure was solved by direct methods (SHELXTL-Plus 4.11/v) and anisotropically refined. H atoms were included in the refinement as riding models with fixed isotropic temperature factors. Drawing made using SHELXTL-Plus graphics package. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See, 'Instructions to Authors', Issue No. 1.

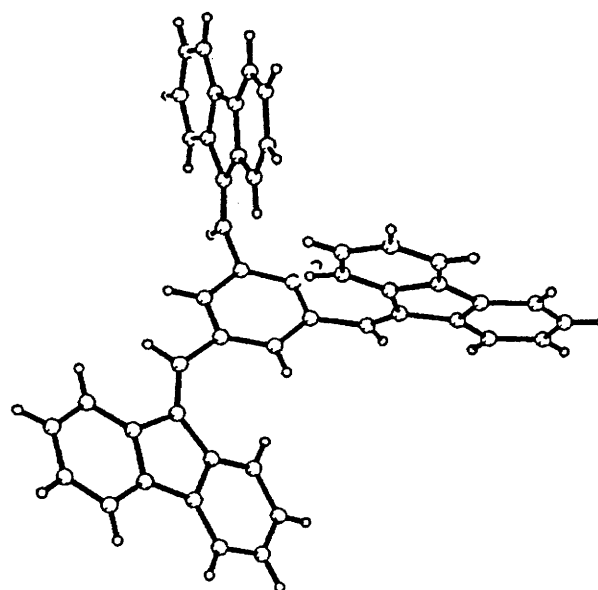


Fig. 1 X-Ray crystal structure of 3

Acknowledgements

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