

Triphenyltruxenene: a C₄₈ Polycyclic Buckybowl Precursor

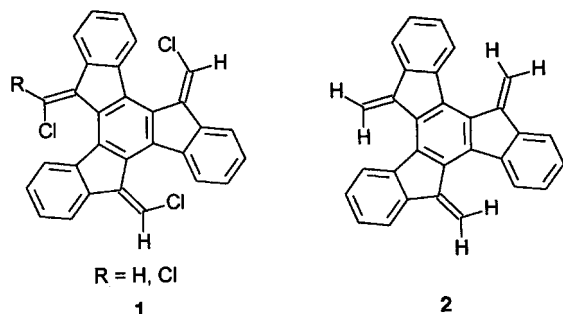
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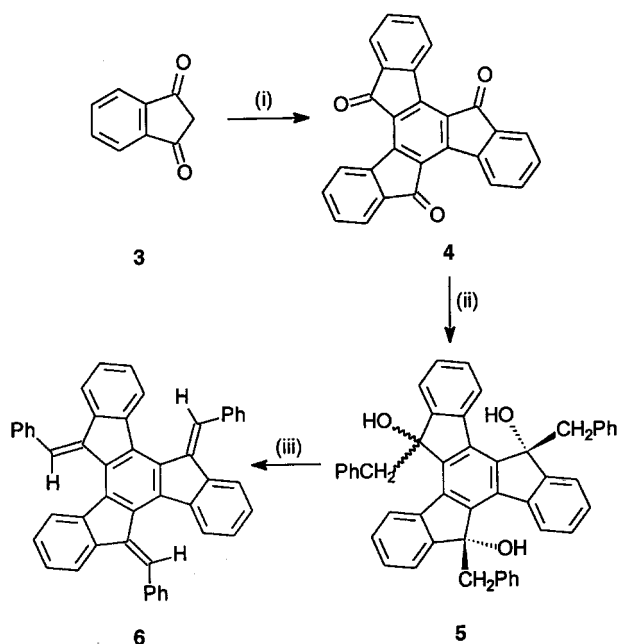
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The synthesis and X-ray crystal structure of the title compound are reported.

The discovery of the fullerenes has led to a renaissance of interest in the synthesis of strained non-planar fragments whose structures represent sections of the buckminsterfullerene surface.¹ Most notable is the synthesis by Rabideau of the C₃₀ fragment semibuckminsterfullerene or hemifullerene by the pyrolysis of a mixture of tri- and tetra-chlorotruxenenes **1**.² This key fragment represents half of the C₆₀ surface and has the correct carbocyclic framework for two enantiomeric halves to dimerise into the C₆₀ cage.³ A previous attempt to prepare hemifullerene by the pyrolysis of truxenene **2** proved unsuccessful.⁴ Truxenene derivatives and their chemistry are clearly of great interest as a route to 'buckybowl' precursors. With this in mind we have prepared triphenyltruxenene **6** and obtained an X-ray crystal structure.



Truxenequinone **4** was prepared (see Scheme) by the acid-catalysed cyclotrimerisation of indane-1,3-dione **3**.⁴ Addition of benzylmagnesium bromide to truxenequinone **4** gave a mixture of the two isomeric alcohols **5** which were readily dehydrated to give triphenyltruxenene **6** by treatment with



Scheme Reagents, conditions and yields: i, conc. H₂SO₄, room temp., 24 h, 75%; ii, PhCH₂MgBr, THF, room temp., 8 h, 99%; iii, TsOH, C₆H₆, heat, 2 h, 56%

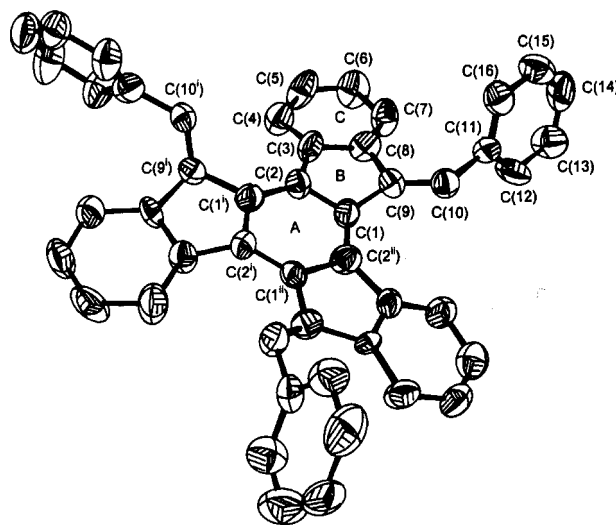


Figure Perspective drawing of triphenyltruxenene showing the crystallographic atom-numbering scheme and 40% probability thermal vibration ellipsoids

toluene-*p*-sulfonic acid in refluxing benzene. In contrast to the poor stability of truxenene **2** and the difficulty in preparing it owing to the reactive exocyclic methylene groups,⁴ triphenyltruxenene **6** is a thermally stable crystalline solid. Owing to the successful pyrolytic synthesis of hemifullerene from **1** by three consecutive ring couplings, the X-ray crystal structure of compound **6** was of particular interest to determine the distances between the coupling sites and to determine the preferred ground-state geometry. Truxenenes can exist in two diastereoisomeric conformations with the lowest-energy conformer calculated to have the three exocyclic alkenes projecting on the same face.⁴ For truxenene **2** the conformer with two alkenes projecting on one face and the other on the opposite side was calculated at the *ab initio* 3-21G level to be 2.52 kcal mol⁻¹ less stable. The perspective drawing of the X-ray crystal structure (Figure) shows the molecules to possess a three-fold symmetry axis perpendicular to the best plane of the central six-membered ring. Each alkene group projects onto the same face, as expected from the calculations for truxenene **2**,⁴ and the alkene bond C(9)—C(10) makes a dihedral angle of 22° to the bond C(2ⁱⁱ)—C(1) of the central benzene ring [C(2ⁱⁱ)—C(1)—C(9)—C(10)]. The carbon atoms of the ring-coupling position C(4)—C(10ⁱ) are fairly close at 3.221(15) Å. Interestingly, the central benzene ring A displays a regular alternation in the bond lengths with C(1)—C(2), C(1ⁱ)—C(2), C(1ⁱ)—C(2ⁱⁱ) and C(1ⁱⁱ)—C(2ⁱⁱ) all 1.418(6) Å and C(1)—C(2ⁱⁱ), C(1ⁱ)—C(2) and C(1ⁱⁱ)—C(2ⁱⁱ) all 1.387(6) Å.

We are currently continuing our studies into the synthesis of halogenated polycyclic derivatives of triphenyltruxenene **6** which may serve as useful precursors to the hemifullerene core.

Crystal Data for 6.—C₄₈H₃₀, *M_r* = 606, *F*(000) = 1908, rhombohedral, *a* = 17.457(5), *c* = 19.134(6) Å, *V* = 5050 Å³, space group *R*3c, (No. 161), *Z* = 6, *D_x* = 1.197 g cm⁻³, μ(MoKα) = 0.063 mm⁻¹. The experimental data were collected at room temperature on a Nicolet P3 diffractometer using a graphite monochromator with MoKα radiation

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($\lambda = 0.71069 \text{ \AA}$). The structure was solved by direct methods.⁵ The final R value was 0.062 ($R_w = 0.043$). The estimated standard deviations for the geometrical parameters involving non-hydrogen atoms lie within the following ranges: bond lengths 0.006–0.015 \AA ; bond angles 0.6–1.0°.

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Techniques used: IR, ^1H and ^{13}C NMR, mass spectrometry, X-ray crystallography

References: 9

Schemes: 1

Table 1: Atomic coordinates and U_{eq} values for non-hydrogen atoms

Table 2: Interatomic distances and angles

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