

# Crystallographic characterization of the helical diketone, C<sub>36</sub>H<sub>14</sub>O<sub>2</sub>, a new product from the flash vacuum pyrolysis of decacyclene in the presence of oxygen

Saeed Attar, David M. Forkey,<sup>†</sup> Marilyn M. Olmstead and Alan L. Balch\*<sup>‡</sup>

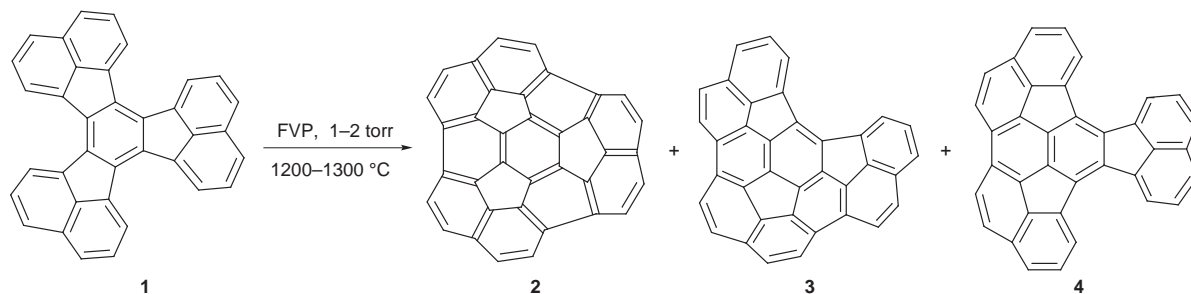
Department of Chemistry, University of California, Davis, California 95616, USA

The helical diketone, C<sub>36</sub>H<sub>14</sub>O<sub>2</sub>, is formed during the flash vacuum pyrolysis of decacyclene in the presence of oxygen and has been characterized by X-ray crystallography.

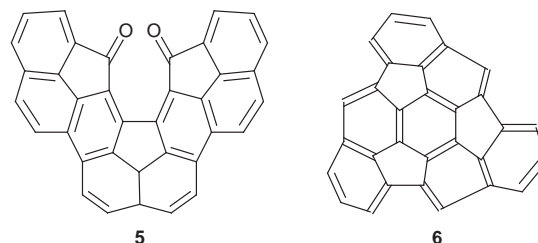
The synthesis and properties of non-planar, polycyclic hydrocarbons that mimic structural motifs within the fullerenes have recently received considerable attention.<sup>1</sup> While the chemical reactivity of the fullerenes themselves is so far largely confined to reactions on the outer surface of the molecule,<sup>2</sup> the availability of fullerene-shaped hydrocarbons allows the exploration of the chemical behavior of not only the convex exterior but also the concave interior as well as the edges of these curved molecules. The high temperature (1250 °C) flash vacuum pyrolysis (FVP) of decacyclene **1**, as described by Scott and co-workers, produces the fullerene-shaped hydrocarbon C<sub>36</sub>H<sub>12</sub> **2**, along with two related products, **3** and **4**, as shown in Scheme 1.<sup>3</sup> Crystallographic characterization of **2** reveals that its structure closely resembles that of C<sub>60</sub>, with a degree of pyramidalization of the central carbon atoms at the base of the bowl that slightly exceeds that of the fullerene but with some outward splaying at the rim of hydrogenated carbon atoms.<sup>4</sup> Here we describe the identification of another product, the helical diketone **5**, that can form in this pyrolytic process through oxidation.

During several preparations of **2** by flash vacuum pyrolysis of decacyclene with subsequent chromatographic separation of the soluble products,<sup>3</sup> we noted that the contents of the second chromatographic band, the one that usually contained the doubly closed bowl **3**, changed when air leaked into the pyrolysis system. Further examination of this band revealed the presence of a new compound, the diketone **5**, (*Chem. Abstr.*, Index Name, cyclopenta[*pqr*]naphth[2',1',8':5,6,7]-*as*-indaceno[1,2,3,4-*tuva*]picene-15,16-dione) which was produced in yields of ca. 0.3–0.5%.

The dione **5** has been fully characterized *via* both spectroscopic<sup>§</sup> and X-ray crystallographic data. Because of the similarities in molecular symmetry and structure, the dione **5** and the doubly closed bowl **3** show comparable but different features in their <sup>1</sup>H NMR spectra. Orange crystals of C<sub>36</sub>H<sub>14</sub>O<sub>2</sub>·1.125 CH<sub>2</sub>Cl<sub>2</sub>·0.75 MeOH·0.25 H<sub>2</sub>O readily form through the diffusion of MeOH into CH<sub>2</sub>Cl<sub>2</sub> solution of the compound.<sup>¶</sup> Two views of the molecule are shown in Fig. 1. Bond distances within the molecule are given in Table 1.



Scheme 1



Although the molecule has no crystallographically imposed symmetry, it is divided into two nearly identical halves with an approximate two-fold axis that passes through the C(13)–C(33) bond. The two C–O distances are consistent with the diketone

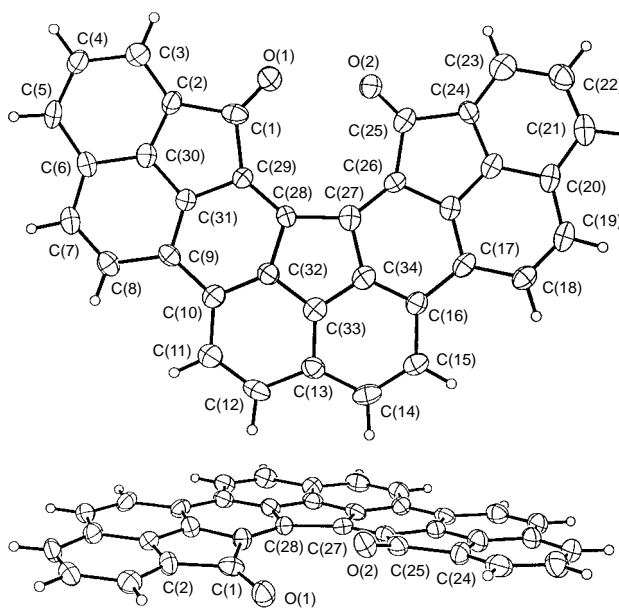
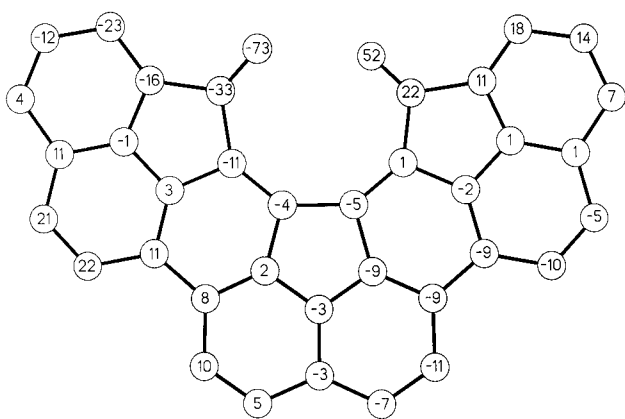


Fig. 1 A perspective view of an isolated molecule of C<sub>36</sub>H<sub>14</sub>O<sub>2</sub> with 50% thermal contours. The top view looks down on the nearly flat surface of the molecule while the lower view emphasizes the non-planarity and helicity of the region near the two oxygen atoms.

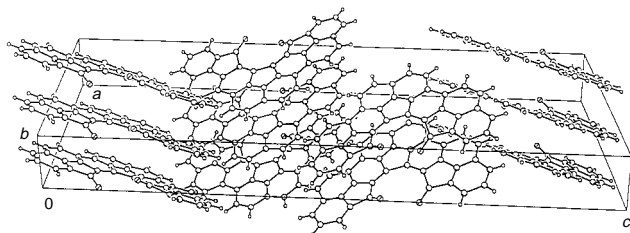
**Table 1** Bond lengths for C<sub>36</sub>H<sub>14</sub>O<sub>2</sub>

Bond	Distance/Å	Bond	Distance/Å
O(1)–C(1)	1.205(7)	O(2)–C(25)	1.204(7)
C(1)–C(2)	1.526(9)	C(24)–C(25)	1.528(8)
C(2)–C(3)	1.366(8)	C(23)–C(24)	1.354(9)
C(3)–C(4)	1.421(9)	C(22)–C(23)	1.422(9)
C(4)–C(5)	1.378(8)	C(21)–C(22)	1.371(9)
C(5)–C(6)	1.421(8)	C(20)–C(21)	1.419(9)
C(6)–C(7)	1.412(8)	C(19)–C(20)	1.428(9)
C(7)–C(8)	1.368(9)	C(18)–C(19)	1.363(9)
C(8)–C(9)	1.461(8)	C(17)–C(18)	1.452(8)
C(9)–C(10)	1.443(8)	C(16)–C(17)	1.441(8)
C(10)–C(11)	1.425(8)	C(15)–C(16)	1.441(8)
C(11)–C(12)	1.372(9)	C(14)–C(15)	1.366(9)
C(12)–C(13)	1.440(8)	C(13)–C(14)	1.436(9)
C(1)–C(29)	1.526(8)	C(25)–C(26)	1.516(8)
C(28)–C(29)	1.371(8)	C(26)–C(27)	1.375(8)
C(27)–C(28)	1.514(8)	C(24)–C(26)	1.396(9)
C(2)–C(30)	1.403(8)	C(20)–C(36)	1.411(8)
C(6)–C(30)	1.415(8)	C(26)–C(35)	1.436(8)
C(29)–C(31)	1.449(8)	C(17)–C(35)	1.399(8)
C(9)–C(31)	1.382(8)	C(35)–C(36)	1.406(9)
C(30)–C(31)	1.401(8)	C(27)–C(34)	1.460(9)
C(28)–C(32)	1.436(8)	C(16)–C(34)	1.385(8)
C(10)–C(32)	1.399(8)	C(33)–C(34)	1.392(8)
C(32)–C(33)	1.395(8)	C(13)–C(33)	1.390(8)

**Fig. 2** Deviations (in 0.01 Å) of the atomic positions from the mean molecular plane for C<sub>36</sub>H<sub>14</sub>O<sub>2</sub>

formulation, and the four immediately adjacent C–C bonds are the longest C–C bonds in the molecule. The dione **5** is not planar but has a slight helical twist, as shown in the lower part of Fig. 1. This helicity arises from the juxtaposition of the two oxygen atoms, which bend away from one another to avoid unduly close contact. The non-bonded O...O distance in **5** is 2.708 (6) Å. Fig. 2 shows the distances of the various carbon atoms from the mean plane of the carbon atoms in **5**. Although individual molecules of **5** are chiral, each crystal is a racemate of the two *M* and *P* enantiomers.

In the solid state, the individual molecules of **5** pack in columns along the *b* axis as shown in Fig. 3. Within each

**Fig. 3** A view of the solid state packing in C<sub>36</sub>H<sub>14</sub>O<sub>2</sub>

column, all molecules have like chirality. However, there are inversion centers between the columns, so that adjacent columns have opposite chiralities. The packing conforms to the β motif, which is one of the four packing arrangements found for polynuclear aromatic hydrocarbons.<sup>5,6</sup> The motif is characterized by a short *b* screw axis and graphitic planes. The β motif is the one utilized by polynuclear aromatic hydrocarbons that are, like the diketone **5**, non-planar.

The formation of the diketone **5** during our flash vacuum pyrolysis of decacyclene has been traced to a leak in the gas inlet system that allowed air to enter the gas stream during pyrolysis. It is likely that **5** formed from oxidation of the doubly closed bowl **3**, since **5** and **3** are related by cleavage of one of the C–C bonds on the periphery of the corannulene-like portion of **3**. However, as indicated by mass spectroscopic and NMR data, the doubly closed bowl **3** is not converted into **5** during the general workup of the pyrolysis products, nor does exposure of a solution of **3** to one atmosphere of O<sub>2</sub> in CHCl<sub>3</sub> solution for 30 min under room light lead to the formation of the dione **5**. Those pyrolysis reactions that produced **5** yielded little or none of the doubly closed bowl **3**, but did produce **2**. The C–C bonds on the edges of these non-planar hydrocarbons are subject to considerable strain, and as the present case reveals, cleavage of just one such bond in **3** can result in the formation the nearly planar dione **5**, with considerable release of strain. In a related study, cleavage of a carbon–carbon bond on the periphery of the semibuckminsterfullerene, C<sub>30</sub>H<sub>12</sub> **6**, has been observed in its reaction with (Ph<sub>3</sub>P)<sub>2</sub>Pt(C<sub>2</sub>H<sub>4</sub>).<sup>7</sup> Clearly the chemistry of these non-planar hydrocarbons that are related to fullerenes deserves continued attention,<sup>8</sup> and reactivity at the edges is likely to be a prominent feature.

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## Notes and References

† On leave from the Department of Chemistry, California State University, Sacramento, CA 95819, USA.

‡ E-mail: albalch@ucdavis.edu

§ Selected data for **5**: δ<sub>H</sub>(300 MHz; CDCl<sub>3</sub>) 7.98 (d, 2 H, *J* 9.0), 7.93 (d, 2 H, *J* 7.2), 7.74 (d, 2 H, *J* 8.7), 7.61 (d, 2 H, *J* 8.7), 7.59 (d, 2 H, *J* 8.1), 7.40 (d, 2 H, *J* 9.0), 7.39 (dd, 2 H, *J* 8.1 and 7.2); ν<sub>max</sub>/cm<sup>-1</sup> 1720 (C=O); *m/z* 478.5 (M<sup>+</sup>).

¶ Crystal data for **5**: Orange needles of C<sub>36</sub>H<sub>14</sub>O<sub>2</sub>·1.125 CH<sub>2</sub>Cl<sub>2</sub>·0.75 MeOH·0.25 H<sub>2</sub>O, clinic, space group *P*2<sub>1</sub>/*c*, *a* = 17.469(4), *b* = 3.8213(8), *c* = 38.627(9) Å, β = 95.18(2)°, *T* = 130(2) K, *Z* = 4, Cu-Kα radiation (λ = 1.54178 Å). Refinement of 3372 reflections and 406 parameters yielded *w*R<sub>2</sub> = 0.2138 for all data and a conventional *R*<sub>1</sub> = 0.071 based on 2120 reflections with *I* > 2σ(*I*). The largest peak and hole in the final difference map are 0.40 and -0.57 e Å<sup>-3</sup>. CCDC 182/865.

In contrast, crystals of the doubly closed bowl, C<sub>36</sub>H<sub>4</sub> **3**, precipitate as orange needles with a hexagonal form. A data set was collected with the crystal indexed in the trigonal *R* crystal system; *a* = *b* = 20.076 (4), *c* = 4.2691 (8) Å. Attempts to solve the structure failed, probably because of twinning.

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