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Hiroki Amano^a, Hidehiro Uekusa^a, Yuji Ohashi^a, Hidetoshi
Tokuyama^a & Eiichi Nakamura^a

^a Department of Chemistry, Tokyo Institute of Technology, Tokyo,
Japan

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STRUCTURE OF FULLERENE ANCHORED BY FIVE-MEMBERED-RING

HIROKI AMANO, HIDEHIRO UEKUSA, YUJI OHASHI,
HIDETOSHI TOKUYAMA and EIICHI NAKAMURA
Department of Chemistry, Tokyo Institute of Technology, Tokyo, Japan

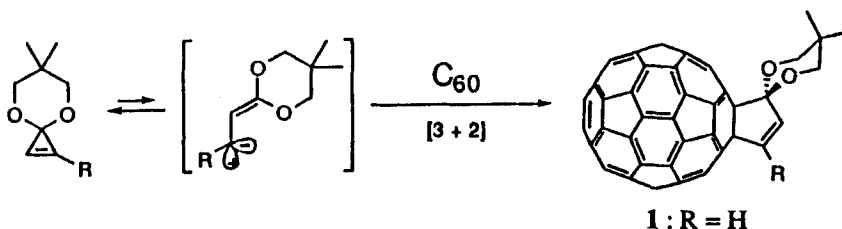
Abstract The X-ray crystal structure of propanofullerene derivative **1** obtained by [3+2] cycloaddition has been determined by X-ray analysis.

INTRODUCTION

C_{60} fullerene has been shown to be a good dienophile and a dipolarophile.¹ Wudl and the coworkers showed that the reactions of diazoalkane provided σ - or π -homoaromatic fullerenes with methano bridge.

The vinylcarbene species generated thermally from cyclopropanone acetal are unique source of carbenes. The vinylcarbene species performs [3+2] cycloaddition reaction with more electron-deficient olefins to generate cyclopentenone derivatives.²

So we applied [3+2] cycloaddition reaction to fullerenes with vinylcarbene species to provide the fullerene anchored by a five-membered-ring as follows;



In order to confirm the above reaction scheme, the fullerene derivative, propanofullerene, in case of $R = H$, was crystallized and its structure was analyzed by X-rays.

RESULTS AND DISCUSSION

The crystals of **1** were obtained as black prisms by recrystallization from a carbon disulfide - *n*-hexane solution. The crystal data are as follows; $C_{68}H_{12}O_2 \cdot CS_2$, $M_r = 936.91$, Orthorhombic, *Pbcn*, dimensions $0.4 \times 0.3 \times 0.15 \text{ mm}^3$, $a = 38.909(6)$, $b = 13.476(1)$, $c = 14.523(1) \text{ \AA}$, $V = 7615(1) \text{ \AA}^3$, $Z = 8$, $D_x = 1.634 \text{ Mg m}^{-3}$, $Cu K\alpha$ radiation, $\lambda = 1.54184 \text{ \AA}$, Cell parameters from 22 reflections, $\theta = 12.5 - 17.5^\circ$, $\mu = 1.761 \text{ mm}^{-1}$, $T = 296 \text{ K}$. The structure was solved by the direct method and refined by the full-matrix least-squares, non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were calculated geometrically and refined isotropically. The final *R* value became 0.084.

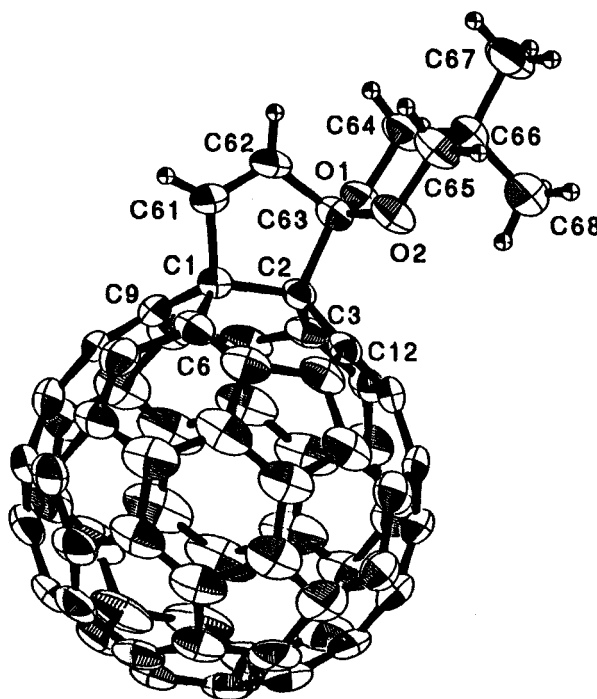


FIGURE 1 Molecular structure of **1**

The molecular structure of **1** is shown in Figure 1. The analyzed structure clearly indicates that the vinylcarbene attacks the connecting $C=C$ double bond of the two six-membered rings of fullerene and forms a five-membered-ring as shown in the scheme.

TABLE I Comparison of the observed and normal bond lengths.

bond	observed/Å	normal/Å
C1 – C61	1.53(1)	(1.51)
C61 – C62	1.31(1)	(1.32)
C62 – C63	1.51(1)	(1.51)
C2 – C63	1.59(1)	(1.54)
C63 – O1	1.40(1)	(1.43)
C63 – O2	1.41(1)	(1.43)
O1 – C64	1.44(1)	(1.43)
O2 – C65	1.43(1)	(1.43)
C64 – C66	1.50(1)	(1.54)
C65 – C66	1.51(1)	(1.54)
C66 – C67	1.53(1)	(1.54)
C66 – C68	1.54(1)	(1.54)

The observed bond lengths of the anchored moiety are compared with the normal ones³ in Table 1. The corresponding values between observed and normal are in good agreement with each other within experimental error. The bond lengths between the two bridged C-atoms C1 and C2 of **1** is 1.58(1) Å. The corresponding bond lengths in the similar structure of the fullerene anchored by a five-membered-ring including N and O atoms⁴ and the fullerene anchored by a three-membered-ring, methanofullerene⁵ are 1.58(1) Å and 1.61(1) Å, respectively. These three values are in good agreement with each other within experimental error. Besides, the four sp^3 — sp^2 bonds, C1 – C6, C1 – C9, C2 – C3, C2 – C12 (1.55(1) Å, 1.52(1) Å, 1.52(1) Å, 1.53(1) Å, respectively) of **1** and the corresponding bonds of methanofullerene are almost same lengths within experimental error.

The crystal structure viewed along the *c* axis is shown in Figure 2. This crystal contains carbon disulfide as solvent. There are two kinds of CS₂; an ordered one and three disordered ones, the central atom being commonly occupied. All the molecules are located on the two-fold rotation axis along the *b* axis.

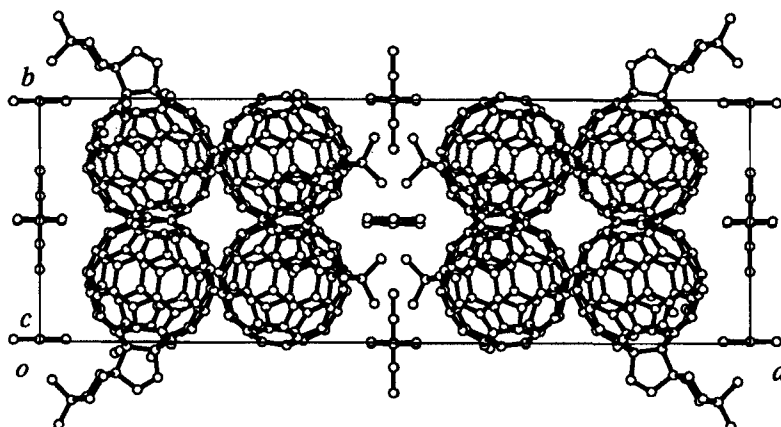


FIGURE 2 Crystal packing of 1

SUMMARY

We applied [3+2] cycloaddition reaction with vinylcarbene species to provide the fullerene anchored by a five-membered-ring. In order to confirm this reaction, the fullerene derivative, propanofullerene, in case of R = H, was crystallized.

The analyzed structure by X-rays clearly indicates that the vinylcarbene attacks the connecting C = C double bond of the two six-membered rings of fullerene and forms a five-membered-ring.

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