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# Isolation and Characterization of Unsymmetrical $C_{60}Me_5O_3H$, a Cage-Opened Bisepoxide Ketone: Tautomerism Involving a Fullerene Cage Bond

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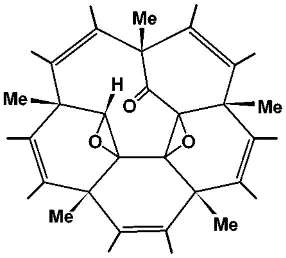
## ABSTRACT



**Bisepoxide ketone $C_{60}Me_5O_3H$, possessing a nine-membered hole in the cage, has been isolated from the reaction of $C_{60}Cl_6$ with methyllithium followed by hydrolysis. It is a tautomer of the recently isolated bisepoxide fullerenol, this tautomerism being the first example involving a cage C–C bond, and may be driven by cage strain. Like the fullerenol, the ketone gives a high $C_{58}^+$ fragmentation ion intensity during EI mass spectrometry.**

The formation of cage-opened fullerene ketones was first conjectured by Chiang et al. to account for the carbonyl stretching frequencies observed with some hydroxylated fullerenes (fullerenols) on treatment with acid.[1] The observed carbonyl stretching frequencies of the ketones (believed to be derived from hemiketals moieties in the fullerenols) were at unusually high wavenumbers (1722 and 1726 cm$^{-1}$). This is attributable to the strain in the fullerene cage, an explanation invoked by Wudl et al. to account for the C═O frequency (1727 cm$^{-1}$) of a characterized cage-opened ketone formed by oxidation of an *N*-methoxyethoxymethylazahomo-[60]fullerene.[2] Recently we described the isolation and full characterization of $C_s$-symmetric $C_{60}Me_5O_2OH$ (**2**) the first bisepoxy fullerenol.[3] From the same reaction ($C_{60}Cl_6$/MeLi followed by hydrolysis) we have now isolated an unsymmetrical isomer (**1**), a cage-opened ketone formed evidently via a 1,3-tautomeric shift of the hydroxyl hydrogen in the fullerenol.

The reaction was carried out as described previously,[3] and after column chromatography (70−230 mesh silica gel) with toluene (byproducts having been removed with toluene/cyclohexane) the toluene eluent was purified by high-pressure liquid chromatography (HPLC). Use of a 10 mm × 250 mm Cosmosil "Buckyprep" column operated at a flow rate of 4.7 mL min$^{-1}$, with elution either by toluene or toluene/heptane, (1:1 v/v) yielded the ketone **1** in low yield. This

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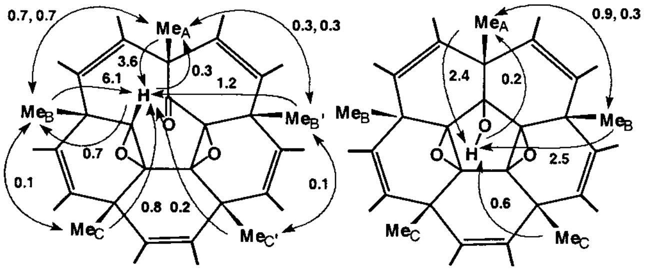
[1] Chiang, L. Y.; Upasani, R. B.; Swirczewski, J. W.; Soled, S. *J. Am. Chem. Soc.* **1993**, *115*, 5453. See also: Chiang, L. Y. in *The Chemistry of Fullerenes*; Taylor, R., Ed.; World Scientific: Singapore, 1995; Chapter 5.

[2] Hummelen, J. C.; Prato, M.; Wudl, F. *J. Am. Chem. Soc.* **1995**, *117*, 7003.

[3] Al-Matar, H.; Hitchcock, P. B.; Avent, A. G.; Taylor, R. *Chem. Commun.* **2000**, 1071.

10.1021/ol0100531 CCC: $20.00



(1) (2)

**Figure 1.** Structures for the ketone $C_{60}Me_5O_3H$ (**1**) and fullerenol $C_{60}Me_5O_2OH$ (**2**) showing NOE couplings (%).

eluted after 5.2 min (toluene) or 10.1 min (1:1 toluene/heptane) [cf. 4.8 min (toluene)/8.8 min (1:1 toluene/heptane) for the fullerenol **2**].

The EI mass spectrum (70 eV, Figure 2) shows the parent ion at 844 amu, and notably, the $C_{58}^+$ fragmentation ion at 696 amu shows an intensity (55%) relative to that of the 720 amu peak, cf. 40% noted for the fullerenol **2**.[3] It arises from the facile loss of 2 CO molecules, which we have noted previously in the mass spectra of phenylated epoxides of [60]fullerene, where the relative intensity was 30%.[4] The loss of both CO and $CO_2$ by thermal fragmentation of fullerene oxides can be monitored by a matrix-isolation technique.[5] It is apparent from the intense 28 and 44 amu peaks in the low mass region of the mass spectrum (inset to Figure 2). (On heating to 250 °C for 3 h, a KBr disk of **1** also showed the formation of the matrix-isolated $CO_2$ band at 2336 $cm^{-1}$.)

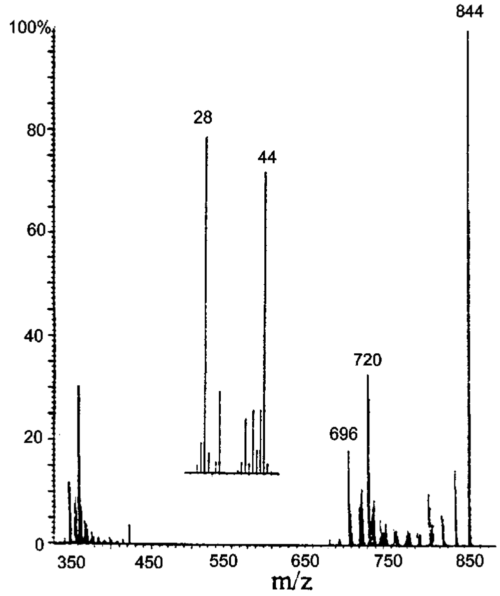


**Figure 2.** EI mass spectrum (70 eV) for $C_{60}Me_5O_3H$ (**1**); inset shows low mass region.

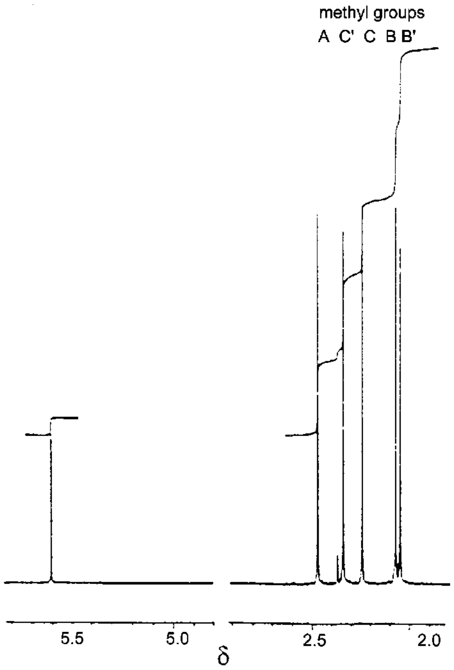


**Figure 3.** $^1H$ NMR spectrum for $C_{60}Me_5O_3H$ (**1**).

The $^1H$ NMR spectrum (Figure 3, $CDCl_3$) shows peaks at $\delta$ 5.60 (1 H, s, cage-H) and 2.37, 2.34, 2.24, 2.08 and 2.04 (each 3 H, s), confirming that the compound is unsymmetrical. [Owing to a lock signal malfunction, the $^1H$ NMR reported[3] resonances for **2** should each be downfield by 0.37 ppm, i.e., at $\delta$ 4.25 (OH), 2.36 ($Me_A$), 2.23 ($Me_C$), and 2.12 ($Me_B$).] The OH peak in **2** and other fullerenols we have isolated ($\delta$ 3.59 and 4.49), all exhibit saturation transfer to water, a reliable test for the presence of OH groups; the peak at $\delta$ 5.60 in **1** (which is significantly further downfield) does not.

The IR spectrum (Figure 4) shows an intense band at 1703 $cm^{-1}$, whereas by contrast the spectrum for **2** shows none, having instead an intense broad band at 3520 $cm^{-1}$.

**Structure of 1.** Salient features in deducing the structure are

(i) it is unsymmetrical;

(ii) the IR spectrum shows a very strong C═O band;

(iii) the NMR singlet at $\delta$ 5.6 is characteristic of hydrogen attached to the cage, e.g., literature values are 5.2 ($C_{60}Ph_5H$, $CS_2$)[6] and 4.5 ($C_{60}Me_5H$, $CDCl_3$);[7]

(iv) the singlet shows no saturation transfer to water and is not therefore part of an OH group;

(v) the NOE couplings (Figure 1) show that the hydrogen giving the singlet must be located (a) *within* the ring of

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(4) Darwish, A. D.; Birkett, P. R.; Langley, G. J.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *Fullerene Sci. Technol.* **1997**, *5*, 705.

(5) Taylor, R.; Penicaud, A.; Tower, N. J. *Chem. Phys. Lett.* **1998**, *295*, 481.

(6) Avent, A. G.; Birkett, P. R.; Crane, J. D.; Darwish, A. D.; Langley, G. J.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1994**, 1463.

(7) Sawamura, M.; Toganoh, M.; Kuminobu, Y.; Kato, S.; Nakamura, E. *Chem. Lett.* **2000**, 270.

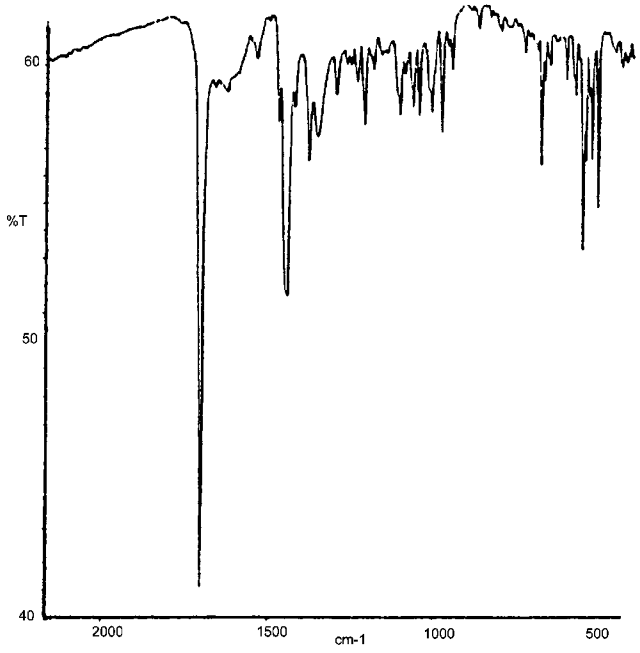

**Figure 4.** IR spectrum (KBr) for $C_{60}Me_5O_3H$ (**1**).

methyl groups, (b) on the central pentagon, (c) *off center*, (d) nearer to $Me_B$ than to $Me_A$.

The data are self-consistent since attachment of H to the cage requires (given the molecular formula) a carbonyl group to be present as observed. Moreover, the chemical shifts of the B/B′ methyls (average 2.06 ppm) in **1** are similar to those corresponding in **2** (2.12 ppm), the shifts for the C/C′ methyls (average 2.29 ppm) are similar to those corresponding in **2** (2.23 ppm), and the shift of the $Me_A$ is the same in each. This indicates similar locations of the methyl groups in each compound. The very weak B/B′ and C/C′ NOE couplings also parallel the insignificant B/C coupling in the (X-ray characterized) **2**.

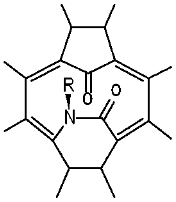

**Figure 5.** Motif present in the *N*-methoxyethoxy-ketolactam derivative of [60]fullerene.

The structure for **1** is the only one either feasible or possible. Furthermore, the carbonyl group is in a six-membered ring and thus is subject to less strain than if it were in a five-membered ring, as in the ketones of Chiang et al.[1] and Wudl and co-workers,[2] and hence appears at a lower wavenumber than in these examples. [Compare also the IR carbonyl frequencies for cyclopentanone (1746 $cm^{-1}$) and cyclohexanone (1714 $cm^{-1}$).[8]]

Isomers **1** and **2** are therefore tautomers and this tautomerism appears to be the first example involving breakage of a fullerene cage C−C bond. It may be driven by reduction of strain in the five-membered central ring of the fullerenol; the bond that breaks in the fullerenol is longer (1.569 Å) than the others in the five-membered ring (1.484 and 1.532 Å).[3]

Finally, the “facing location” of the C═O and C−H groups in **1** has a parallel in the similar locations of C═O and NR (more sterically crowded) in the motif (Figure 5) for the *N*-methoxyethoxy-ketolactam precursor that is the precursor for the formation of aza[60]fullerene.[2]

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[8] *Aldrich Library of FT IR Spectra*; Pouchet, C. J., Ed.; Aldrich: Milwaukee, 1985.