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Fullerene Aziridine. Facile Synthesis and Spectral Characterization of Fullerene Urethane, $C_{60}NCO_2CH_2CH_3$

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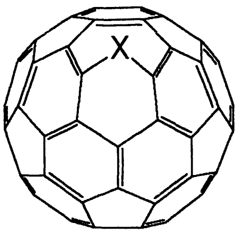
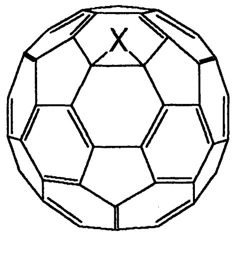
A fullerene urethane, $C_{60}NCO_2CH_2CH_3$, was obtained by a one-pot reaction from C_{60}, NaN_3, $ClCO_2CH_2CH_3$, and 15-crown-5 ether in refluxing toluene. The structure of the product was spectroscopically determined as a closed aziridine at a 6/6-ring junction.

Recently we reported the synthesis, isolation, and characterization of the C_{60} adducts with benzyne, dienes, and dichlorocarbene.1) The structure of the adducts is attracting much attention. Wudl *et al.* reported that open fulleroid **1** (R = H) was obtained by pyrolysis of the diazomethane-C_{60} adduct.2) Smith *et al.* have recently reported closed methanofullerene **2** (R = H) given by photolysis from the same precursor.3) The nitrogen- and oxygen-bridged fullerenes are known only as an open iminoannulene **3**4) and as a closed epoxide form **4**,5) respectively. We report here the synthesis and spectral characterization of closed nitrogen-bridged fullerene **5**, the first fullerene aziridine derivative.



1 X = CR_2
3 NCH_2Ph



2 X = CR_2
4 O
5 $NCO_2CH_2CH_3$

The synthesis was planned to be conducted by a one-pot procedure in order to avoid a potential hazard during the purification of azidoformic ester. A mixture of C_{60} (72 mg), NaN_3 (80 mg, purity 90%), $ClCO_2CH_2CH_3$ (1 mL), 15-crown-5 ether (0.5 mL), and toluene (20 mL) was refluxed for 1 h under argon. By passing a short column of silica gel eluted with 4:1 hexane-toluene (recovering 28.7 mg of C_{60}) and then with toluene, a pink fraction was collected and the solvent evaporated to dryness under reduced pressure to give black solid (47.1 mg). It (12.7 mg) was purified by HPLC equipped with Jaigel 1H+1H columns (Japan Analytical Industry) and eluted with toluene, affording pure **5** (4.7 mg, yield 22%; 96% based on the consumed C_{60}) and C_{60} (6.8 mg) recovered. No significant intermediate was characterized so far under milder conditions.

The EI mass spectrum (70 eV, 270 °C) of **5** showed the molecular ion peak at *m/z* 807 together with a base peak at *m/z* 720 due to the fragment C_{60}. The UV/Vis absorption spectrum6) was similar to those of the fullerene cyclopropanes1c,3,7,8) and epoxide.5) The absence of the absorption of N=N stretching in the IR spectrum9) suggests the loss of nitrogen of the adduct under these reaction conditions. The ^1H NMR spectrum exhibited a typical coupling pattern of an ethoxy group.10) The ^{13}C NMR spectrum (Fig. 1) showed that 15 signals (with one signal unresolved) were observed in the fulleroid region (140-146 ppm), indicating C_{2v} symmetry in the fullerene moiety. The fulleroid carbons are counted up to 58 and the signal at 81.4 ppm can be assigned to quaternary bridgehead carbons. The structure **5** with a closed aziridine structure at a 6/6-ring junction explains satisfactorily all of the spectral data. The rotation around N-C(=O) or the pyramidal inversion

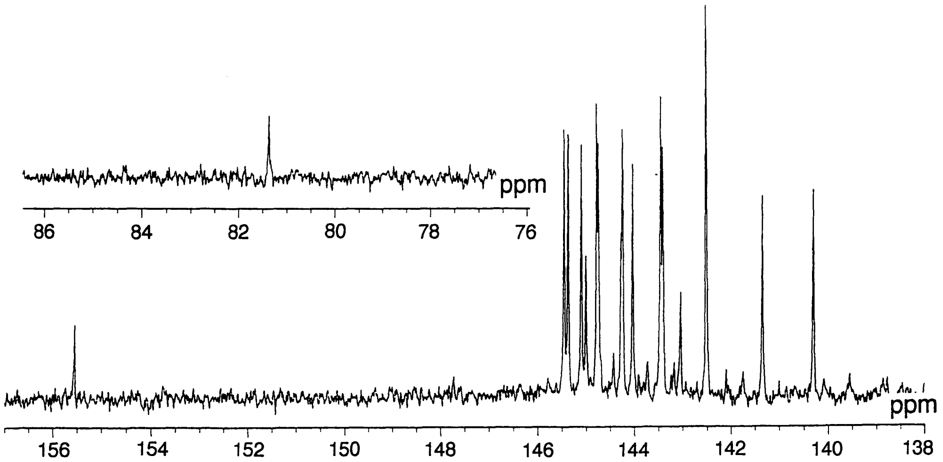


Fig. 1. ^{13}C NMR spectrum of **5** (68 MHz, 25 °C, 4:1 CS_2-C_6D_6) δ 155.6(C=O), 145.44(4), 145.36(4), 145.1(4), 145.0(2), 144.78(4), 144.73(4), 144.27(2), 144.23(4), 144.0(4), 143.44(4), 143.40(4), 143.0(2), 142.5(8), 141.3(4), 140.3(4), 81.4 (2), 64.3 (CH_2, not shown), 14.9 (CH_3, not shown). The carbon abundances shown in parentheses were determined by relative signal integrals. The signal at δ 142.5 was resolved in 3:1 CS_2-$CDCl_3$.

of the nitrogen seems free for the NMR time scale. The cyclic voltammetry of **5** revealed the presence of irreversible process and slight shifts of the reduction potentials from those of C_{60}, as seen in the result of **2** (R = Cl)[1d] (the first peak positions: **5**, -0.94 V; C_{60}, -0.93 V *vs*. Ag/Ag^+. For experimental conditions, see ref. [1d]).

No change was observed in the UV/Vis absorption spectrum of **5** after refluxing in *o*-dichlorobenzene for 8 h. This fact suggests the thermodynamic stability of the closed skeleton. The thermal isomerizations from **1** to **2** were reported (CR_2 = CPh_2,[11] $CHCO_2Et$[12]), indicating that the closed structure is more stable than the open one. The substituents on the bridge facilitate the isomerization.[11,12] In the case of nitrogen analog, the similar results were obtained; the presence of a carbonyl group in conjugation with the nitrogen bridge may favor to afford thermodynamically stable isomer **5**, in contrast to the result that the reaction with an alkyl azido reagent gave only **3**.[4] Mechanistic investigation and further derivatizations of **5** are now in progress.

References

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6) UV/Vis (CH_2Cl_2) λ_{max}/nm 257 (log ε 5.2), 324 (4.6), 410 (3.4), 421 (3.3), 494 (3.1), 680 (sh, 1.7).
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9) IR (KBr disk) 1740, 1420, 1400, 1225, 1180, 1090, 1035, 525 cm^{-1}.
10) ^{1}H NMR (270 MHz, 25 °C, 4:1 CS_2-C_6D_6) δ 4.40 (q, *J* = 7.0 Hz, 2H), 1.37 (t, *J* = 7.0 Hz, 3H).
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