Adduct of C70 at the Equatorial Belt: Photochemical Cycloaddition with Disilirane[1]

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Organic chemical derivatizations of fullerenes such as C_{60} and C_{70} by addition reactions are intensely attractive to chemists. Although many derivatives of C_{60} have now been investigated,[2,3] only a few discrete individual products of C_{70},[4] such as metal complexes[5] and alkylated fullerenes,[6] have been isolated and characterized. While all positions in C_{60} are identical, five sets of carbon atoms (labeled a–e in Figure 1) and eight distinct types of C–C bonds are available in C_{70}.[7] It can be anticipated that the different bonds display different reactivities.[7] In both the reaction of C_{70} with $[Ir(CO)Cl(PPh_3)_2]$ to give $[(\eta^2\text{-}C_{70})Ir(CO)\text{-}Cl(PPh_3)_2]$[5a] and the hydroalkylations of C_{70},[6] attack occurs at the most reactive double bonds (a–b bond) at the poles. Similarly, the osmylation of C_{70} takes place regioselectively at sites of greater local curvature like the a–b bond.[5b]

Although photoinduced charge transfer between C_{70} and electron donors such as aromatic amines,[8] semiconductor colloid,[9] and ascorbate[10] can occur, there has so far been no example of formation of a photoadduct. In this communication, we report the novel photochemical reaction[11] of C_{70} with a disilirane[12] affording a cycloadduct as the first silylated C_{70}. This is the first example in which addition occurs at the equatorial belt (e–e bond).

A toluene solution of C_{70} (3.3×10^{-3} M) and 1,1,2,2-tetramesityl-1,2-disilirane[12] (1, 3.3×10^{-3} M) was photolyzed with a high-pressure mercury-arc lamp (cutoff < 300 nm) to afford a thermally stable 1:1 adduct (2) with complete consumption of C_{70} (Scheme 1). Adduct 2 can be isolated readily in 85% yield by preparative HPLC. No thermal cycloaddition occurs at elevated temperatures up to 100 °C.

Figure 1. Side view of C_{70} showing sets of identical carbon atoms labeled a–e.

Figure 2. (a) UV–vis spectra of C_{70} (- - -) and 2 (—) from 190 to 820 nm in hexane. (b) Time-dependent spectral changes of a toluene solution of C_{70} and 1 upon irradiation.

Scheme 1

FAB mass spectrometry of 2 ($C_{107}H_{46}Si_2$) displays a peak for 2 at 1390–1386 as well as one for C_{70} at 843–840 which arises from loss of 1. The UV–vis absorption spectrum of 2 is virtually identical to that of C_{70} except for subtle differences in the 350–550 nm region (Figure 2a). 2 exhibits a new band at 407 nm but lacks the C_{70} bands at 381 and 471 nm. Photochemical changes in the absorption spectra are shown in Figure 2b.

The FAB mass and UV–vis spectra of 2 contain a number of unique features, but also suggest that this new fullerene retains the essential electronic and structural character of C_{70}.

The ^{1}H NMR spectrum of 2 displays six methyl signals at 3.08, 2.20, 2.17, 1.99, 1.95, and 1.75 ppm and four meta-proton signals on the mesityl groups at 6.75, 6.63, 6.58, and 6.52 ppm.[13] A singlet for the methylene protons at 1.83 ppm is also observed. The ^{13}C NMR spectrum[13] of 2 shows 35 signals for the C_{70} skeleton: one at 60.61 ppm and the remainder between 128 and 160 ppm.[14] The former signal is attributed to the sp^3 fullerene carbons. Twelve signals for four tertiary and eight quarternary carbon atoms, six signals for methyl carbon atoms, and one signal for the methylene carbon atom of the disilirane component are

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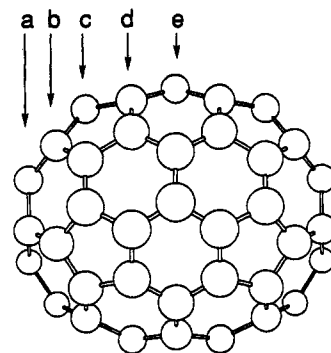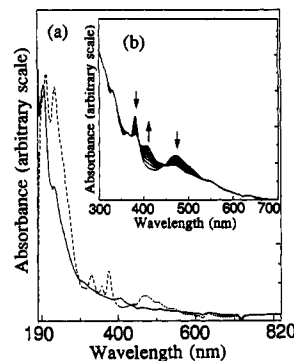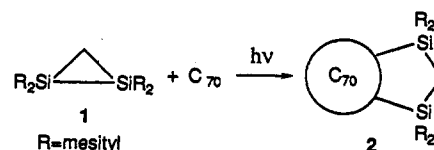(12) Ando, W.; Kako, M.; Akasaka, T.; Nagase, S. *Organometallics* **1993**, *12*, 1514.

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(14) ^{13}C NMR (125 MHz, $CS_2/CD_2Cl_2 = 3:1$): δ 159.37, 150.13, 149.78, 148.94, 148.56, 148.45, 148.29, 147.68, 147.43, 147.41, 147.16, 146.95, 146.81, 146.17, 146.04, 145.54, 145.26, 145.23, 144.84, 144.47, 143.78, 143.72, 143.35, 142.20, 141.42, 141.08. 140.76, 140.68, 140.54, 139.69, 139.42, 139.38, 138.30, 137.39, 134.46, 134.25, 133.60, 133.09, 132.10, 131.82, 130.34 (*m*-H), 130.17 (*m*-H), 129.97 (*m*-H), 128.87, 128.10 (*m*-H). Overlapping might obscure one signal.

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Table 1. Isomers of **2** and Their Symmetries

isomer (bond index of C_{70})[a]	5-membered ring	symmetry	CH_2	Si	$C(sp^3)$ on C_{70}
a—a bond (1.105)	planar	C_s	x	o	o
	bent	C_s	x	o	o
	twist	C_1	x	x	x
a=b bond (1.480)	planar	C_s	o	x	x
	bent	C_1	x	x	x
	twist	C_1	x	x	x
b—c bond (1.109)	planar	C_1	x	x	x
	bent	C_1	x	x	x
	twist	C_1	x	x	x
c=c bond (1.526)	planar	C_s	x	o	o
	bent	C_s	x	o	o
	twist	C_1	x	x	x
c—d bond (1.066)	planar	C_1	x	x	x
	bent	C_1	x	x	x
	twist	C_1	x	x	x
d=d bond (1.302)	planar	C_s	x	o	o
	bent	C_s	x	o	o
	twist	C_1	x	x	x
d=e bond (1.306)	planar	C_1	x	x	x
	bent	C_1	x	x	x
	twist	C_1	x	x	x
e—e bond (1.094)	planar	C_{2v}	o	o	o
	bent	C_s	x	o	o
	twist	C_2	o	o	o

[a] Calculated with the AM1 method. [b] o = equivalent; x = nonequivalent.

also observed. In the H–C COSY NMR spectrum, a cross peak corresponding to the methylene protons at 1.83 ppm and the methylene carbon atom of the disilirane component at 9.82 ppm was observed. The ^{29}Si NMR spectrum of **2** shows a peak at –15.88 ppm, which is assigned to the silicon atom of **2**.[3a,13] Table 1 shows the isomers of 1:1 adducts of C_{70} and **1** and the equivalency of NMR signals in them. In order to obtain further information on the structure of **2**, a variable temperature ^1H NMR measurement was carried out.[15] Coalescence of the meta-proton signals at 85 °C reflecting conformational change of the molecule was observed, yielding an activation energy of $\Delta G^{\ddagger}$ =18.1 kcal/mol.[16] This result reveals the equivalency of aromatic protons above the coalescence temperature, indicative of (a) 1,2-addition across a 6,6-ring junction at the equatorial belt (e–e bond) or (b) 1,4-addition at the same position. These spectral data and Table 1 suggest C_2 symmetry of **2** in which the conformation of the five-membered ring is twisted around an sp^3 carbon–carbon bond of the fullerene component.

The equatorial bonding structure for **2**, in which either 1,2-adduct (**2a**) or 1,4-adduct (**2b**) structures are conceivable, was confirmed by AM1 molecular orbital calculation;[17] these C_2 structures correspond to energy minima. The structures of **2** obtained by full geometry optimization at the AM1 level are shown in Figure 3; four bulky mesityl groups are beautifully spaced in C_2 symmetry with the observed equivalency. The high barrier observed is ascribed to the fact that the space between C_{70} and mesityl groups as well as between mesityl groups becomes filled upon transformation from one twist conformer to the other. An exact assignment of the isomers, however, may await X-ray structural determinations.

The free energy change (ΔG) for electron transfer from **1** to the triplet state of C_{70} is 11.3 kcal/mol.[18] The rate of disappearance of C_{70} was suppressed by addition of 10 equiv of

(15) The mixed solvent, $CS_2/CD_3C_6D_5$ = 1:5, was used.

(16) $\Delta G^{\ddagger}$ values were calculated according to the Eyring equation.

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(18) The ΔG value was calculated according to the Rehm–Weller equation[21] (ΔG = 23.06[$E(D/D^+) - E(A^-/A) - \Delta E_{0,0} - 0.74^{22}$]) by using the oxidation potential of **1** (0.81 V vs SCE),[12] the reduction potential of C_{70} (–0.37 V vs SCE),[23] and the triplet energy of C_{70} (1.43 V).[24]
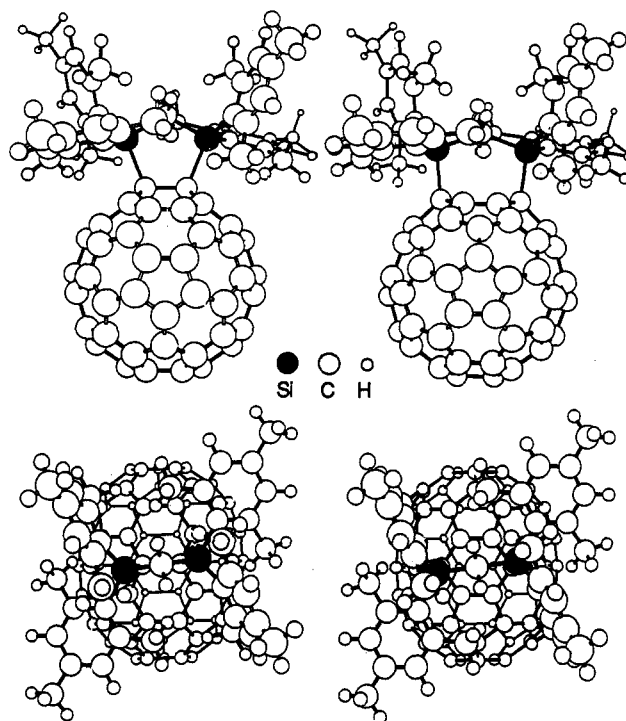

Figure 3. Two views of the optimized C_2 structures of **2a** (left) and **2b** (right) calculated with the AM1 method.

diazabicyclo[2.2.2]octane (E_p = 0.70 V vs SCE)[19] and 100 equiv of 1,2,4,5-tetramethoxybenzene (E_p = 0.79V vs SCE),[19] each of which has a low oxidation potential and is unreactive to photoreaction by C_{70}. The reaction was inhibited by addition of 10 equiv of rubrene as triplet quencher. The fact that this adduct is also formed upon irradiation at >400 nm where C_{70} is the only light-absorbing component indicates that C_{70} triplet, which is known to be efficiently produced from C_{70} singlet, undergoes interaction with the ground state of **1** forming an exciplex intermediate.[3a,20]

On the basis of the symmetry derived from the spectral data, **2** is the first isolated product of addition across an equatorial belt (e–e bond) in C_{70}. The reason for the observed regioselectivity on this photocycloaddition of C_{70} is unknown at the present time. Further studies on the reaction mechanism are in progress.

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