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Photochemical Bissilylation of C_{60} with Disilane[1]

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The photochemical reaction of C_{60} with disilane **1** affords the adduct **2** as a bissilylated product. The unique redox properties of **2** are reported by means of differential pulse voltammetry. The compound **2** was characterized by NMR, IR, and UV−vis spectroscopies. Spectroscopic and theoretical investigation strongly support the 1,16-addition structure having C_2 symmetry which results from addition at the 1,16 positions in C_{60}. The results are reasonably accounted for by the generation of a silyl radical which is responsible for the formation of **2**.

Introduction

Organic chemical derivatization of C_{60} with nucleophiles, radicals, dienes, dipoles, organometallic reagents, electrophiles, and so forth, continues to yield fascinating results.[2] To design new organofullerenes for applications in material science and biochemistry, one should know their electronic properties, namely their redox properties. We showed that reduction and oxidation potentials have good linear correlations with the LUMO and HOMO energy levels, respectively, on the basis of a comparative electrochemical study of various organofullerenes derivatized with oxygen-, carbon-, and silicon-containing groups at a 6,6-ring junction.[3,4] Among these organofullerenes, a characteristic feature of the monosilylated and bissilylated fullerenes is their higher reduction and lower oxidation potentials than C_{60} itself and than analogous carbon substituted derivatives, which are the result of the electron-releasing nature of silicon relative to carbon. This result can be confirmed by a theoretical calculation indicating that almost 1 electron is transferred onto C_{60} from the silicon substituents.[3] In this context, we report here the strikingly low oxidation potential of the bissilylated C_{60} obtained in the photochemical reaction of C_{60} with a disilane. The yields of this addition are also good with respect to synthetic fullerene chemistry.

Scheme 1

$$C_{60} + \underset{\mathbf{1}}{(RR'_2Si)_2} \xrightarrow[\text{benzene}]{h\nu} \underset{\mathbf{2}}{(RR'_2Si)_2C_{60}}$$

a: R = tBu, R' = Ph
b: R = R' =Ph
c: R = H, R = Ph

Results and Discussion

Irradiation of a benzene solution of 1,1,2,2-tetraphenyl-1,2-di-*tert*-butyl-1,2-disilane (**1a**, 2.0×10^{-3} M) and C_{60} (2.0×10^{-3} M) with a low-pressure mercury-arc lamp in a quartz tube resulted in formation of the adduct **2a** in 58% yield (Scheme 1). The adduct **2a** can be readily isolated by preparative HPLC. Similar results were also obtained with hexaphenyldisilane (**1b**) and 1,1,2,2-tetraphenyldisilane (**1c**). FAB mass spectrometry of **2a** ($C_{92}H_{38}Si_2$) displays a peak for the compound at 1202−1198 as well as one for C_{60} at 723−720 which arises from loss of two $^tBuPh_2Si$ groups. The UV−visible absorption spectrum of **2a** is virtually identical to that of C_{60} except for a subtle difference in the 400−650-nm region. These results suggest that **2a** retains the essential electronic and structural character of C_{60}.

The ^1H NMR spectrum of **2a** displays ortho proton signals of the phenyl groups at 8.00 and 7.93 ppm, along with a multiplet signal for the other phenyl protons and a singlet for two ^tBu groups. The ^{13}C NMR spectrum of **2a** shows 30 signals in almost equivalent intensities for the C_{60} skeleton: one at 65.71 ppm and the remainder between 165 and 130 ppm. The former signal is assigned to the sp^3 fullerene carbon atoms. The ^{29}Si spectrum of **2a** shows a peak at −3.53 ppm. In addition, analysis of ^{13}C NMR and 2D NMR (CH−COSY and long-range CH−COSY) also disclosed the presence of the two diaste-

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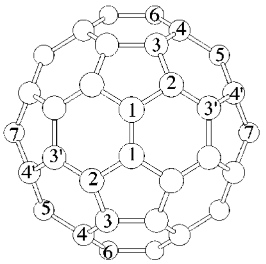
Table 1. The Relative Heat of Formation (kcal/mol) and Number of Double Bonds at the 5,6-Junction of 3a−i



compd	position of addition	relative heat of formation[a]	number of double bonds at 5,6 junction
3a	1−1	0.0	0
3b	2−2	19.9	4
3c	3−3	38.6	6
3d	3′−3′	4.6	2
3e	4−4	36.4	6
3f	4′−4′	39.3	8
3g	5−5	23.8	4
3h	6−6	47.8	8
3i	7−7	36.4	10

[a] Calculated at AM1 level.

reotopic phenyl groups. These spectral data clearly indicate that **2a** has C_2 symmetry.

We carried out the AM1 molecular orbital calculation[5] of several bissilylated C_{60} derivatives, which would provide some clues in understanding the structure of **2a**. Table 1 shows nine possible isomers of $(H_3Si)_2C_{60}$ (**3a−i**) with C_2 symmetry, accompanied by the corresponding relative heats of formation and the number of double bonds at the 5,6-junction. The 1,2-adduct **3a** was found to be most stable among these isomers. The 1,6-adduct[6] **3d** is 4.6 kcal/mol less stable than **3a**. It is readily understandable that **3b−i** have disadvantages, given that they have more than one double bond localized within the more highly strained five-membered rings.[7] On the other hand, the 1,2-adduct of $(^tBuPh_2Si)_2C_{60}$ will be significantly destabilized by steric congestion caused by the two bulky $^tBuPh_2Si$ groups. The 1,6-adduct was calculated to be most stable among $(^tBuPh_2Si)_2C_{60}$ isomers, being more stable than the corresponding 1,2-isomer by 35.6 kcal/mol; **2a** is best represented by the 1,6-adduct structure.[8] The optimized structure of 1,6-$(^tBuPh_2Si)_2C_{60}$ at the AM1 level is shown in Figure 1.

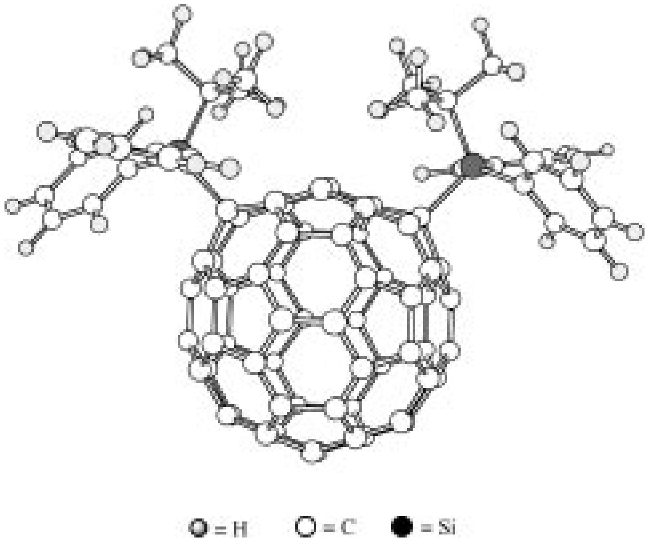


Figure 1. Optimized structure of **2a**.

Recently we reported on the photochemical bissilylation of C_{60} via its excited state.[4b] To shed light on the mechanism of the reaction of **1** with C_{60}, 532-nm-laser photolysis with observation of transient absorption bands in the near-IR region was carried out.[9] The absorption band of $^3C_{60}{}^*$ at 740 nm was observed immediately after the laser exposure. The decay of $^3C_{60}{}^*$ was not accelerated upon the addition of disilane **1**. The absorption band of $C_{60}{}^{\cdot -}$, which was anticipated would appear at 1070 nm,[9a,c−e] was not observed at all. Thus, it is evident that $^3C_{60}{}^*$ and $C_{60}{}^{\cdot -}$ do not play an important role in these reactions. These results indicate that the formation of **2a** might be rationalized in terms of the intermediacy of $^tBuPh_2Si^\bullet$ radical generated by photochemical Si−Si cleavage of **1a**. In fact, none of **2a** was produced upon irradiation at >300 nm where the cleavage of **1a** does not take place. This radical mechanism is further substantiated by the formation of $^tBuPh_2SiCl$ and Cl_3CCCl_3 in the photolysis of **1a** and C_{60} in the presence of CCl_4. When the reaction was carried out in the radical scavenger cumene, the yield of **2a** was suppressed along with the formation of $(SiPh_2{}^tBu)HC_{60}$, which was detected by means of mass spectrometry. It has been known that the UV photolysis of **1a** produces $^tBuPh_2Si^\bullet$ almost exclusively, giving slight amounts of silatriene and silene byproducts.[10] In contrast, no silylated C_{60} product was obtained in the photolysis of C_{60} with $(MePh_2Si)_2$ (**1d**), $(Me_2PhSi)_2$ (**1e**), or $(^iPrPh_2Si)_2$ (**1f**). These results for **1d−f** might be attributable to inhibition of silyl-radical addition to C_{60} caused by the concomitant reactions such as disproportionation of silyl radicals and intramolecular 1,3-silyl migration.[11] In the case of **1e**, the corresponding disproportionated product, Me_2PhSiH, was actually observed by means of mass analysis.

As shown in Table 2, **2a** and the related bissilylated compounds **4** (1,2-adduct)[2] and **5** (1,4-adduct)[12] showed three reversible reductions and two irreversible oxidations in 1,2-dichlorobenzene as observed before.[3] The salient feature is that 1,6-adduct **2a** has a remarkably low oxidation potential (+0.33 V) as compared to **4** (+0.77 V) and **5** (+0.73 V). The theoretical calculation (3-21G//AM1)[13] is in agreement with this result; the ionization

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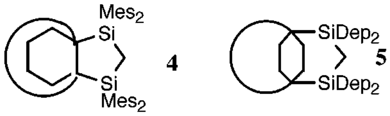
Table 2. Redox Potentials [V] and HOMO and LUMO Levels [eV] of 2a, 4, and 5[a]



Mes = 2,4,6-trimethylphenyl
Dep = 2,6-diethylphenyl

compd	oxE$_2$[b,c]	oxE$_1$[b,c]	redE$_1$	redE$_2$	redE$_3$	HOMO[d]	LUMO[d]
C_{60}		+1.21	−1.12	−1.50	−1.95	−9.64	−2.95
1,2-adduct **4**[e]	+1.22	+0.60	−1.29	−1.67	−2.18	−8.68	−2.49
1,4-adduct **5**	+1.26	+0.73	−1.22	−1.61	−2.12	−8.66	−2.52
1,6-adduct **2a**	+1.20	+0.33	−1.19	−1.59	−2.18	−8.35	−2.66

[a] Half-cell potentials unless otherwise stated. Values are relative to ferrocene/ferrocenium couple. [b] Irreversible. [c] Values were obtained by DPV. [d] Calculated at AM1 level. [e] Reference 3.

Table 3. The Relative Energies (kcal/mol) and Ionization Potentials (I_p, eV) of 3a, 3d, and 3j, Their Cation Radicals[a]

isomer	neutral	cation radical	I_p
1,2-adduct **3a**	3.4	7.4	7.26
1,4-adduct **3j**	0	0	7.09
1,6-adduct **3d**	14.5	−1.4	6.40

[a] Calculated at 3-21G//AM1 level.

potentials of $(H_3Si)_2C_{60}$ decrease in the order 1,2-adduct **3a** (7.26 eV) > 1,4-adduct **3i** (7.09 eV) > 1,6-adduct **3d** (6.40 eV) as shown in Table 3. This dramatic result for the electrochemical properties could be explained by the unique structure of the 1,6-adduct: the 1,6-adduct has two short bonds between a pentagon and a hexagon, which gives more strain to the carbon framework[7] (Figure 2). This strain energy may be released in the cationic form where these bonds (1.450 Å by AM1) are much longer than those in the neutral form (1.387 Å by AM1).

In conclusion, it has been demonstrated that bissilylation of C_{60} takes place readily via silyl radicals generated photochemically from simple disilanes. Experimental data and theoretical calculation suggest that the redox properties of fullerenes are controlled not only by the electronegativity of the substituents but also by the regiochemistry of functionality and its effect on their network. It is expected that these derivatized fullerenes, which display strikingly low oxidation potentials, will open up new applications of C_{60} as an electron donor.

Experimental Section

Gel permeation chromatographic separation was performed on an LC-918 recycling preparative HPLC (Japan Analytical Industry Co., Ltd.) with a series of Jaigel 1H and 2H columns in which toluene was used as eluant.

Cyclic voltammetry experiments were performed at 1 mM analyte concentration in 1,2-dichlorobenzene with 0.1 M Bu_4NPF_6, an $Ag/AgNO_3$ (CH_3CN) reference electrode, and a Pt-disk working electrode. Ferrocene (0.5 mM) was added as an internal reference. The scan rate was 20 mV/s. Difference pulse voltammetry experiments were carried out under the same conditions used for CV measurement. Pulse amplitude, pulse width, and pulse period were 50 mV, 50 ms, and 200 ms, respectively. The scan rate was 20 mV/s.

AM1 and ab initio 3-21G molecular orbital calculations were carried out using the Gaussian 94 program.[13]

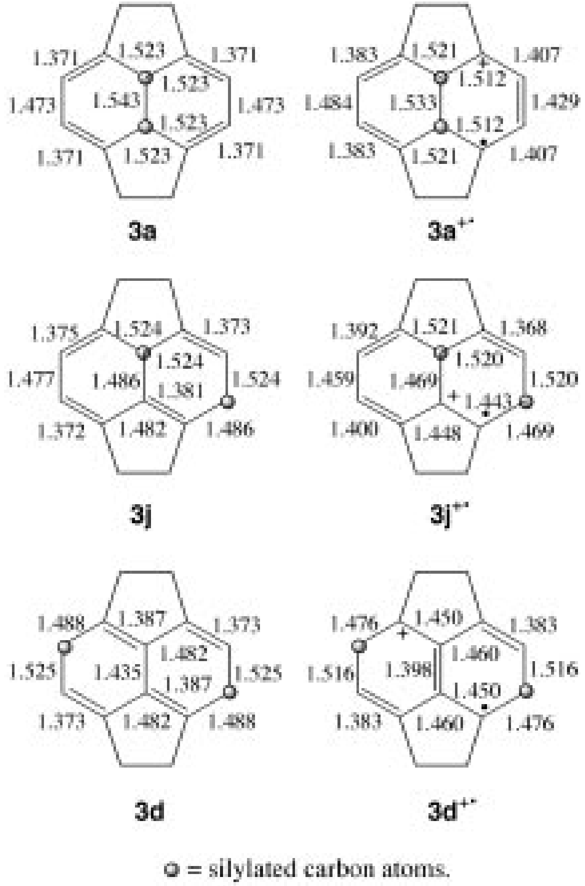


Figure 2. Selected bond lengths on neutral and cationic **3a**, **3d**, and **3j** calculated by the AM1 method.

Photolysis of 1,1,2,2-Tetraphenyl-1,2-di-*tert*-butyldisilane (1a) with C_{60}. A benzene solution of 1,1,2,2-tetraphenyl-1,2-di-*tert*-butyl-disilane (**1a**, 2.0 × 10^{-3} M) and C_{60} (2.0 × 10^{-3} M) was irradiated with a low-pressure mercury-arc lamp in aquartz tube for 2 h. The solvent was removed by a rotary evaporator. The adduct **2a** was isolated by preparative HPLC in 58% yield.

Compound **2a**: dark brown solid; ^{1}H NMR $(CS_2/CD_2Cl_2/500$ MHz) 8.00 (4H, dd, J = 10.1, 1.6 Hz), 7.93 (4H, dd, J = 10.1, 1.6 Hz), 7.45−7.25 (12H, m), 1.46 (18H, s) ppm; ^{13}C NMR $(CS_2/CD_2Cl_2/125$ MHz) 163.63 (s), 161.81 (s), 152.66 (s), 149.99 (s), 148.48 (s), 147.69 (s), 146.89 (s), 146.80 (s), 146.63 (s), 146.23 (s), 146.01 (s), 145.97 (s), 145.81 (s), 145.75 (s), 145.69 (s), 145.40 (s), 144.35 (s), 143.74 (s), 143.34 (s), 142.34 (s), 142.04 (s), 142.03 (s), 141.42 (s), 141.20 (s), 140.56 (s), 139.41 (s), 138.69 (s), 137.39 (d), 137.25 (d), 136.61 (s), 136.54 (s), 130.95

(s), 130.93 (s), 130.07 (d), 130.01 (d), 127.61 (d), 127.49 (d), 65.71 (s), 30.29 (q), 23.42 (s) ppm; ^{29}Si NMR (CS_2/CD_2Cl_2/99.3 MHz) −3.53 ppm; FABMS (toluene/NBA) *m*/*z* 1198 (M)$^+$, 720 (C_{60})$^+$; UV−vis (hexane) λ_{max} (nm) 248, 283, 335, 461. Anal. Calcd for $C_{92}H_{38}Si_2{\cdot}{}^1/_2CS_2$: C, 89.70; H, 3.17. Found: C, 88.63; H, 3.28.

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