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Synthesis, X-ray Structure, and Properties of the Singly Bonded C_{60} Dimer Having Diethoxyphosphorylmethyl Groups Utilizing the Chemistry of C_{60}^{2-}

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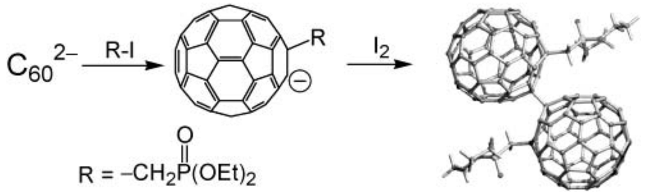
ABSTRACT



A singly bonded C_{60} dimer having a diethoxyphosphorylmethyl group on each C_{60} cage was obtained by the reaction of C_{60}^{2-} dianion with diethyl iodomethylphosphonate followed by the treatment with iodine. The precise structure of the dimer was determined for the first time by X-ray crystallography, and its homolytic dissociation as well as spectroscopic and electrochemical properties were clarified.

The singly bonded fullerene dimers $RC_{60}-C_{60}R$ are of interest for their unusual structures with a C−C single bond carrying such large cage fragments at both ends and also as a model of C_{60} polymers.[1] After the pioneering work by Krusic and co-workers, there have been many experimental and theoretical studies on these dimers.[2] Generally, they are formed by coupling of $RC_{60}^{\bullet}$ radicals, which in turn are generated in situ by addition of a $R^{\bullet}$ radical to C_{60}. One such example is the radical reaction of C_{60} with perfluoroalkyl iodides in the presence of $(R_3Sn)_2$ upon photoirradiation.[3]

On the other hand, the C_{60}^{2-} dianion is a strong electron donor and a potential nucleophile to react with electrophiles such as organic halides.[4] The reaction mechanism was studied in detail by Fukuzumi and co-workers;[5] they demonstrated that the reaction takes place by way of electron transfer followed by an S_N2 reaction. In addition, the recent studies by Cousseau and co-workers have shown that the chemically generated C_{60}^{2-} dianion can be a versatile precursor in the synthesis of a variety of functionalized C_{60} derivatives.[6] Herein, we report the synthesis of a novel singly bonded C_{60} dimer having a diethoxyphosphorylmethyl group on each C_{60} cage by the use of C_{60}^{2-} dianion chemistry and the first X-ray crystal structure of this singly bonded dimer.

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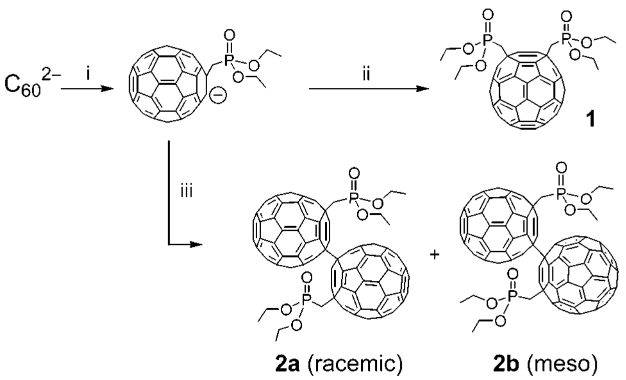
The C_{60}^{2-} dianion was generated by the chemical reduction of C_{60} with CH_3SNa (2.4 equiv) in acetonitrile under an argon atmosphere.[6a] When 25 equiv of diethyl iodomethylphosphonate was added, the deep red color of C_{60}^{2-} changed immediately to dark green. The NIR spectrum showed absorptions at 630 and 956 nm, indicating the formation of the monoanion RC_{60}^- ($R = CH_2PO(OEt)_2$). Because of the bulkiness of the attached phosphonate group, the monoanion was kinetically stabilized and did not undergo further reaction with an excess of diethyl iodomethylphosphonate at room temperature. However, at higher temperature (50 °C), with a larger excess of diethyl iodomethylphosphonate (50 equiv) and after a reaction time of 24 h, a product that showed a correct molecular ion peak for 1,4-bisadduct **1** in HRMS (FAB) was obtained in 10% yield[7] (Scheme 1), while 14% of C_{60} was recovered unchanged. The results of the theoretical calculations by B3LYP/3-21G* revealed that, among the three isomers with 1,2-, 1,4-, and 1,6-bisaddition patterns, the 1,4-bisadduct is the most stable one, i.e., 4.4 kcal mol^{-1} more stable than the 1,2-bisadduct and 11.4 kcal mol^{-1} more stable than the 1,6-bisadduct. In agreement with these results, the ^{1}H NMR of the product confirmed that only the 1,4-bisadduct was formed. For example, the protons of CH_2 groups bonded to the C_{60} core exhibited eight-line signals as a diastereotopic AB system coupled with the phosphorus atom. In addition, the ^{13}C NMR showed 31 signals for the sp^2 carbons of the C_{60} cage indicating that this is a 1,4-bisadduct having the C_s symmetry.

Scheme 1[a]



[a] Reaction conditions: (i) $ICH_2PO(OEt)_2$ (25 equiv), CH_3CN, rt, 5 min; (ii) $ICH_2PO(OEt)_2$ (25 equiv), 50 °C, 24 h; (iii) I_2 (2 equiv).

When the monoanion RC_{60}^-, generated in the same way as above, was treated with I_2, a brown precipitate was immediately formed. After separation by flash chromatography and further purification by preparative gel-permeation chromatography, singly bonded dimer **2** (**2a** + **2b**),[8] which showed the correct molecular ion peak by APCI MS, was obtained in 42% yield, while 34% of C_{60} was recovered unchanged. The dimer **2** was apparently formed by coupling of the monomer radicals produced by one-electron oxidation of the monoanion by I_2. Although the directly bonded fullerene dimers generally have poor solubility,[2d,h,3,9] dimer **2** is highly soluble in common organic solvents such as CS_2, toluene, and $CHCl_3$, owing to the presence of two polar phosphonate groups.

The UV−vis spectrum of dimer **2** in chloroform was virtually identical to that of 1,4-bisadduct **1** as shown in Figure 1, with a broad absorption at 447 nm, which is diagnostic to the 1,4-bisadduct.[10] Thus, the C_{60} cages in dimer **2** were considered to be connected also at the 1,4-positions. The ^{31}P NMR spectrum displayed two signals at 22.99 and 22.95 ppm in a ratio of 1:1.70, indicating that dimer **2** consists of two inseparable isomers in this ratio, which would correspond to racemic and meso forms or vice versa (Scheme 1). According to the values of heat of formation calculated by PM3, the racemic isomer was found to be more stable

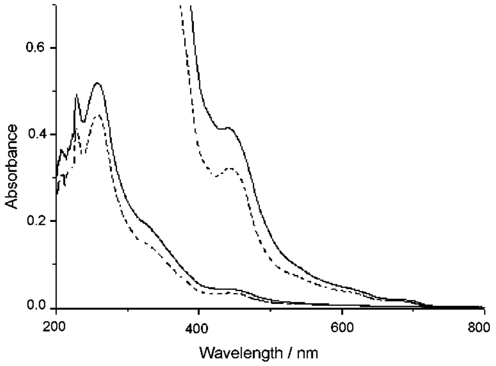


Figure 1. UV−vis spectra of 1,4-bisadduct **1** (dotted line, 4.30 × 10^{-5} M) and dimer **2** (solid line, 3.34 × 10^{-5} M) in $CHCl_3$.

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[7] Spectral data of 1,4-bisadduct **1**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.36−4.25 (m, 8H), 3.67 (dd, 2H, $J = 15.6$ Hz, $^2J_{P-H} = 17.7$ Hz), 3.55 (dd, 2H, $J = 15.3$ Hz, $^2J_{P-H} = 17.1$ Hz), 1.40 (dt, 12H, $J = 7.20$ Hz, $^4J_{P-H} = 3.3$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.06, 155.02, 150.82, 160.68, 148.66, 147.82, 147.15, 147.04, 147.01, 146.90, 145.56, 145.53, 145.41, 145.17, 144.69, 144.37, 144.28, 144.21, 143.99, 143.64, 143.47, 143.25, 143.06, 142.65, 142.60, 142.33, 142.08, 141.61, 140.99, 138.91, 138.57, 62.47 (d, $^2J_{P-C} = 17.7$ Hz), 52.73 (d, $^2J_{P-C} = 4.60$ Hz), 38.68 (d, $^1J_{P-C} = 140.39$ Hz), 16.53 (d, $^3J_{P-C} = 6.33$ Hz); ^{31}P NMR (160 MHz, $CDCl_3$) δ 23.37; UV−vis λ_{max} (log ϵ) ($CHCl_3$) 255 (5.00), 447 (3.73), 678 (2.67); MS (+APCI) m/z 1023.3 (M + H$^+$); HRMS (FAB) calcd for $C_{70}H_{25}O_6P_2$ (M + H$^+$) 1023.1127, found 1023.1161. Upon cyclic voltammetry in *o*-dichlorobenzene, three reversible reduction waves were observed at $E_{1/2} = -1.15, -1.64$, and -2.02 V vs Fc/Fc$^+$.

[8] Spectral data of dimer **2**: ^{1}H NMR (300 MHz, $CDCl_3-CS_2$ (1:1)) δ 4.23−4.08 (m, 8H), 3.84−3.48 (m, 4H), 1.31−1.26 (m, 12H); ^{13}C NMR (75 MHz, $CS_2-C_6D_6$ (6:1)) δ 156.88, 156.78, 154.35, 154.20, 154.08, 154.00, 153.94, 153.86, 150.13, 150.11, 150.01, 149.78, 149.70, 149.73, 149.51, 149.49, 149.32, 149.04, 148.96, 148.49, 148.42, 148.26, 148.00, 147.96, 147.71, 147.66, 146.51, 146.48, 146.37, 146.34, 146.32, 146.27, 145.95, 145.89, 145.58, 145.47, 145.36, 145.31, 145.25, 145.20, 145.17, 145.14, 145.11, 145.06, 144.92, 144.89, 144.74, 144.59, 144.56, 144.39, 144.21, 144.15, 144.10, 144.08, 144.01, 143.98, 143.83, 143.80, 143.59, 143.48, 143.45, 143.39, 143.36, 143.27, 143.23, 142.96, 142.89, 142.85, 132.26, 141.84, 141.80, 140.37, 140.32, 140.22, 139.98, 139.04, 139.00, 67.47, 67.44, 62.63~62.44 (m), 54.47 (d, $^2J_{P-C} = 3.77$ Hz), 40.25 (d, $^1J_{P-C} = 138.75$ Hz), 40.05 (d, $^1J_{P-C} = 138.97$ Hz), 17.40 (d, $^3J_{P-C} = 5.70$ Hz); ^{31}P NMR (160 MHz, $CDCl_3$) δ 22.99, 22.95; UV−vis λ_{max} (log ϵ) ($CHCl_3$) 260 (5.34), 447 (4.21), 687 (2.91); MS (+APCI) m/z 1743 (M + H$^+$).

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than the meso isomer by 1.42 kcal mol^{-1}. Reflecting the presence of two isomers, the ^{13}C NMR spectrum of dimer **2** (Figure 2) displayed two signals for the methylene carbons connected to the C_{60} core at δ 40.05 ppm ($^1J_{P-C}$ = 138.97 Hz) and 40.25 ppm ($^1J_{P-C}$ = 138.75 Hz). The sp^2 carbons in C_{60} cages exhibited more than 76 overlapped signals, indicating that this is a mixture of two isomers.

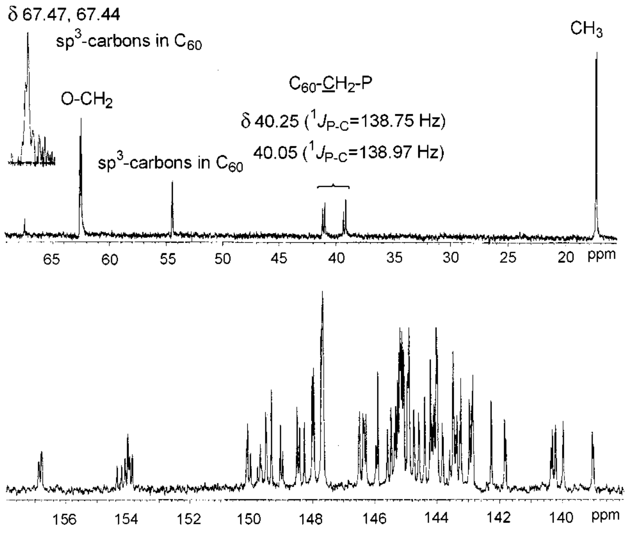

Figure 2. ^{13}C NMR spectrum of dimer **2**: sp^3 carbon range (top) and sp^2 carbon range (bottom).

The precise structure of the dimer was determined by X-ray crystallography for the single-crystal grown in a chloroform solution.[11] This is the first example of an X-ray structure for this kind of singly bonded C_{60} dimer. In each unit cell, there are two independent molecules, which are a mixture of disordered meso and racemic compounds; for the purpose of clarity, the structure of only one molecule, that is, meso isomer **2b**, is shown in Figure 3.

As expected from the UV−vis spectral data, the two C_{60} cages are connected by a single bond at the 1,4-position. The length of the central bond (C1−C1*) connecting the two C_{60} cages is 1.576(6) Å, which is longer than the ordinary $C_{sp3}-C_{sp3}$ bond (1.54 Å). Interestingly, this value is almost identical to the length of the inter-cage bond of the [2 + 2] type doubly bonded C_{60} dimer, C_{120} (1.575(7) Å).[9]

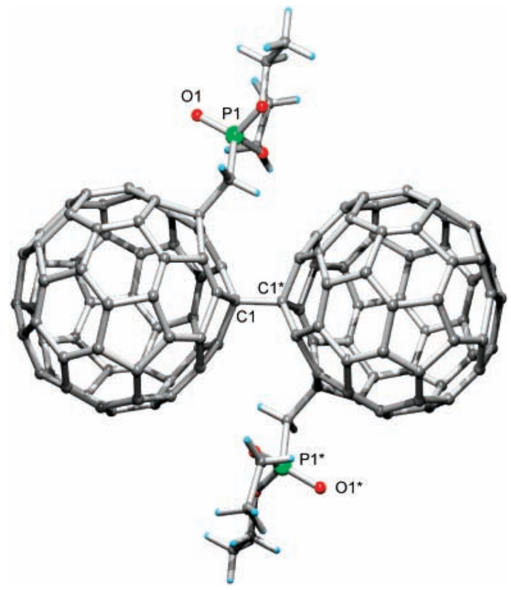

Figure 3. X-ray structure of dimer **2b**.

A solution of this dimer in *o*-dichlorobenzene (ODCB) exhibited an ESR signal at room temperature, indicating that the dimer is in equilibrium with the monomer radical in solution. The unsymmetrical and complicated shape observed for this signal is ascribed to the presence of at least two conformers of the fullerenyl radicals differing in the rotatory position of the phosphorus atom relative to the radical center. However, by elevating the temperature, the rotation around the $C(C_{60})-CH_2$ bond became fast at the ESR time scale, and at 400 K, as shown in Figure 4, an ESR signal was observed as a doublet of triplets due to the coupling with ^{31}P and with CH_2 protons (a_P = 0.96 G, a_H = 0.38 G, g = 2.0023). On the basis of the comparison of the integrated signal intensity of the radical observed for a solution of **2** in ODCB with that of the signal of 2,2-di(4-*tert*-octylphenyl)-1-picrylhydrazyl (DPPH) with a known concentration, the dissociation constant K and the free energy of dissociation ΔG at 27 °C was estimated to be 4.1 × 10^{-10} mol L^{-1} and

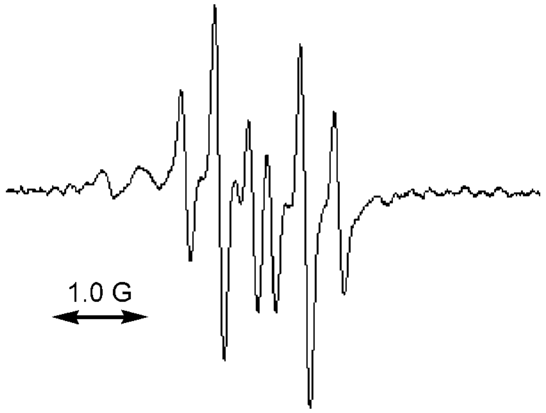

Figure 4. ESR spectrum of the monomer radical dissociated from dimer **2** in a solution in ODCB (2.9 × 10^{-2} M) at 400 K.

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[11] Crystal data for dimer **2**: $C_{130}H_{24}O_6P_2 \cdot 4CHCl_3$, M = 2220.90, crystal in monoclinic, space group $P2(1)/c$, a = 19.810(3) Å, b = 15.450(2) Å, c = 28.723(4) Å, β = 101.230(5)°, V = 8522(2) Å^3, D_{calcd} = 1.711 mg/mm^3, μ = 0.497 mm^{-1}, $F(000)$ = 4456. The measurement was performed on a Bruker SMART APEX diffractometer with Mo Kα radiation and graphite monochromator. 60269 reflections (19734 unique, R_{int} = 0.0468) were collected at 100 K with 1.50 ≤ θ ≤ 27.50°. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL software with a GOF = 1.056. Final wR2 = 0.2564, with a conventional R1 = 0.0988 (reflections with $I > 2\sigma(I)$).

13 kcal mol^{-1}, respectively. By the measurement of temperature dependence of the ESR signal intensity at the temperature range of 380−420 K, the enthalpy of dissociation for **2** was determined as $\Delta H° = 17.0$ kcal mol^{-1}. This value is in accidental agreement with that reported for the dimer $Br_3CC_{60}-C_{60}CBr_3$ (17.0 kcal mol^{-1} determined at 300−375 K).[2a,2b]

The redox property of the dimer **2** was studied by the use of cyclic voltammetry in ODCB (Figure 5). A pair of irreversible redox waves (E_{pc} −1.21 and E_{pa} −0.65 V vs Fc/Fc$^+$) were observed; the cathodic peak at −1.21 V would correspond to the reduction of the monomer radical $RC_{60}^{\bullet}$ formed by the dissociation to the monomer anion RC_{60}^-, while the anodic peak at −0.65 V would correspond to the oxidation of the monoanion RC_{60}^- to the radical followed by rapid recombination to dimer **2**.[12] In addition, two pairs of reversible waves were observed at $E_{1/2}$ −1.60 and −2.04 V, which should correspond to the reduction from RC_{60}^- to RC_{60}^{2-} and from RC_{60}^{2-} to RC_{60}^{3-}, respectively.

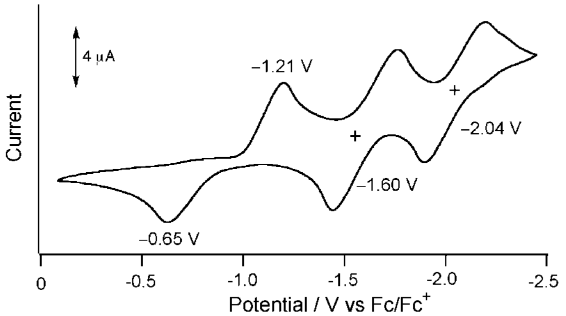

Figure 5. Cyclic voltammogram of dimer **2** (1 mM in ODCB with 0.05 M Bu_4NBF_4, scan rate 0.02 V s^{-1}).

In conclusion, by the reaction of C_{60}^{2-} dianion with diethyl iodomethylphosphonate, followed by one-electron oxidation with iodine, a new singly bonded C_{60} dimer having two phosphonate groups at the 1,4-positions was obtained. By use of spectroscopic methods and by the first X-ray crystallographic study, it was found that the dimer consisted of racemic and meso isomers. The ESR study indicated that about 0.006% of the dimer dissociates into the radical at room temperature at the dimer concentration of 2.9×10^{-2} M, and the bond dissociation enthalpy of the central bond was estimated to be 17.0 kcal mol^{-1}.

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Supporting Information Available: Detailed experimental procedures and crystallographic data for **2b** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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