OH groups and to develop a new generation of sialyl Le^x analogs and mimetics which may have better and more desirable biological activities.

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The Dimerization of RC_{60} Radicals[†]

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Since the discovery, isolation, and characterization of C_{60} and other fullerenes,[1,2] it has become evident that these compounds have a rich and multifaceted chemistry. There are already reports of the alkylation,[3] halogenation,[4] and epoxidation[5] of C_{60} and reports of the addition of $C(C_6H_5)_2$ across its double bonds,[6] in addition to the preparation of organometallic derivatives.[7] In none of these studies, however, has there been any suggestion of concatenation of fullerene molecules, i.e., "necklace" formation of $R(C_{60})_nR$. In the present communication we report the existence of the prototype of such derivatives: dimers of the alkyl–C_{60} radical adducts, which were recently detected by electron spin resonance spectroscopy (ESR).[8]

Alkyl radicals add rapidly and multiply to C_{60} to give products R_nC_{60}, which have been identified by mass spectrometry and, for odd *n*, by ESR spectroscopy.[8,9] With a few notable exceptions (R = H, F, CH_3), a number of monoalkyl radical adducts have been identified unequivocally by the proton and ^{13}C hyperfine structure of their ESR spectra.

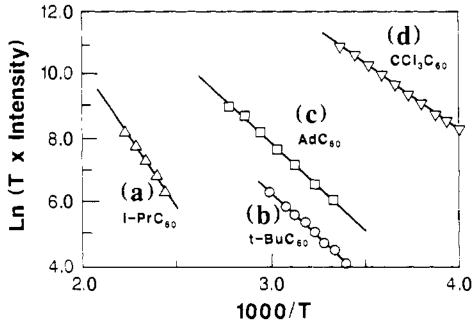

Figure 1. Graphs of ln ($T \times$ intensity) versus $1000/T$ for the spectrum of (a) isopropyl–C_{60}, (b) *tert*-butyl–C_{60}, (c) 1-adamantyl–C_{60}, and (d) CCl_3–C_{60} radicals.

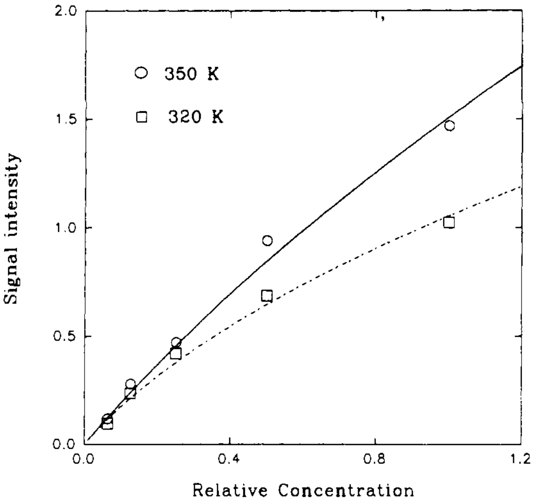

Figure 2. Intensity, in arbitrary units, of the ESR spectrum of *tert*-butyl–C_{60} at 320 and 350 K as a function of relative concentration. The curves are a least-squares fit based on an $R_2 \rightleftharpoons 2R$ equilibrium.[14]

Table I. Isotropic *g* Factors, Proton Hyperfine Interactions (G), and Enthalpies of Dimerization (kcal/mol) of RC_{60} Radicals

R	g factor	HFI	$-\Delta H$	temp/K
$(CH_3)_2CH$	2.002 23	6H = 0.15 1H = 0.48	35.5	420–450^a
$(CH_3)_3C$	2.002 25	9H = 0.17	22.1	300–400^{b,c}
$1\text{-}C_{10}H_{15}{}^d$	2.002 24	6H = 0.05 3H = 0.26	21.5	300–400^{b,c}
CCl_3	2.003 41		17.1	250–310^e
CBr_3	2.009 10		17.0	300–375^f

[a] UV photolysis of RBr in *tert*-butylbenzene.[11] [b] UV photolysis of RBr in benzene. [c] UV photolysis of di-*tert*-butyl peroxide + RH in benzene. [d] 1-Adamantyl. [e] UV photolysis of CCl_4 containing dissolved C_{60}. [f] UV photolysis of CBr_4 dissolved in toluene/C_{60}.

A remarkable feature of the ESR spectra of the RC_{60} adducts was the dramatic increase in intensity of the spectrum with increasing temperature, in contrast to the usual decrease in intensity associated with the Curie law. With $(CH_3)_3CC_{60}$ in benzene, for example,[10-12] the spectral intensity increased by 1 order of magnitude as the temperature was raised from 300 to 350 K, and it decreased again as the temperature was lowered, disappearing at ca. 280 K. This cycle could be repeated several times without significant radical decay, although prolonged heating at 400 K

[†] Du Pont No. 6223; NRCC No. 34192.

(1) Kroto, H. W.; Allaf, A. W.; Balm, S. P. *Chem. Rev.* **1991,** *91,* 1213.

(2) Curl, R. F.; Smalley, R. E. *Science* **1988,** *242,* 1017.

(3) Bausch, J. W.; Surya Prakash, G. K.; Olah, G. A.; Tse, D. S.; Lorents, D. C.; Bae, Y. K.; Malhotra, R. *J. Am. Chem. Soc.* **1991,** *113,* 3205.

(4) (a) Selig, H.; Lifshitz, C.; Peres, T.; Fischer, J. E.; McGhie, A. R.; Romanow, W. J.; McCauley, J. P., Jr.; Smith, A. B., III *J. Am. Chem. Soc.* **1991,** *113,* 5475. (b) Olah, G. A.; Bucsi, I.; Lambert, C.; Aniszfold, R.; Trivedi, N. J.; Sensharma, D. K.; Surya Prakash, G. K. *J. Am. Chem. Soc.* **1991,** *113,* 9385. (c) Tebbe, F. N.; Becker, J. Y.; Chase, D. B.; Firment, L. E.; Holler, E. R.; Malone, B. S.; Krusic, P. J.; Wasserman, E. *J. Am. Chem. Soc.* **1991,** *113,* 9900.

(5) (a) Wood, J. M.; Kahr, B.; Hoke, S. H., II; Dejarme, L.; Cooks, R. G.; Bon-Amotz, D. *J.* Am. *Chem. Soc.* **1991,** *113,* 5907. (b) Creegan, K. M.; Robbins, J. L.; Robbins, W. K.; Millar, J. M.; Sherwood, R. D.; Tindall, P. J.; Cox, D. M.; Smith, A. B., III; McAuley, J. P., Jr.; Jones, D. R.; Gallagher, R. T. *J. Am. Chem. Soc.* **1992,** *114,* 1103.

(6) Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F.; Almarsson, O. *Science* **1991,** *254,* 1186.

(7) (a) Hawkins, J. M.; Meyer, A.; Lewis, T. A.; Loren, S.; Hollander, F. J. *Science* **1991,** *252,* 312. (b) Fagan, P. J.; Calabrese, J. C.; Malone, B. *Science* **1991,** *252,* 312. (c) Fagan, P. J.; Calabrese, J. C.; Malone, B. *J. Am. Chem. Soc.* **1991,** *113,* 9408.

(8) Morton, J. R.; Preston, K. F.; Krusic, P. J.; Hill, S. A.; Wasserman, E. *J. Phys. Chem.* **1992,** *96,* 3576.

(9) (a) Krusic, P. J.; Wasserman, E.; Parkinson, B. A.; Malone, B.; Holler, E. R.; Keizer, P. N.; Morton, J. R.; Preston, K. F. *J. Am. Chem. Soc.* **1991,** *113,* 6274. (b) Krusic, P. J.; Wasserman, E.; Keizer, P. N.; Morton, J. R.; Preston, K. F. *Science* **1991,** *254,* 1184.

(10) Mixtures of C_{60} (ca. 90%) and C_{70} (ca. 10%) were purchased from Texas Fullerenes, Houston, TX. The components were separated chromatographically using activated, neutral alumina (Aldrich) and hexane as the eluent (Taylor, R.; Hare, J. P.; Abdul-Sada, A. K.; Kroto, H. W. *J. Chem. Soc., Chem. Commun.* **1991,** 1423).

(11) In a typical experiment, 10 μL of *tert*-butyl bromide was added to 175 μL of a saturated (ca. 0.002 M) solution of C_{60} in benzene or *tert*-butylbenzene in a 4 mm i.d. Suprasil tube, using a glove box continuously flushed with dry N_2 or Ar. The samples were then irradiated in the cavity of the ESR spectrometer with the focused light of a 1000-W high-pressure Hg/Xe lamp (NRCC) or a 500-W Cermax xenon illuminator (Du Pont). The lamp outputs were filtered through an aqueous $CoSO_4/NiSO_4$ filter. The ESR spectrometers were either a Varian Associates E-102 (NRCC) or a Bruker ESP-300 (Du Pont), both being equipped with the usual devices for readout of the temperature, microwave frequency, and magnetic field.

(12) Excellent spectra were also obtained by irradiation of pivalaldehyde (10 μL), pivalaldehyde (10 μL) and di-*tert*-butyl peroxide (10 μL), or di-*tert*-butyl ketone (10 μL) in saturated benzene solutions of C_{60} (175 μL, ca. 0.002 M). Thermal methods consisted of heating at 330 K either *tert*-butyl peroxypivalate (Lupersol 11) or azoisobutane and C_{60} in benzene in a 1:1 molar ratio.

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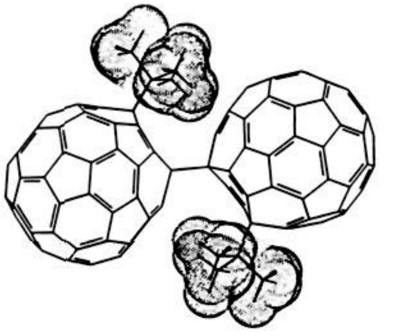


Figure 3. Molecular model of the dimer [*tert*-butyl–C_{60}]$_2$.

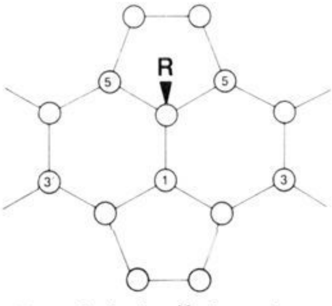
did eventually result in some reduction in signal intensity. Other radical adducts exhibited similar behavior, but in markedly different temperature ranges (Figure 1). Temperature dependence of this type is indicative of an equilibrium between a radical and its dimer, as typified by the behavior of the classical Gomberg radical $(C_6H_5)_3C$.[13]

The dependence of signal intensity on temperature and dilution at a fixed temperature (Figure 2) clearly established that the radical adducts of C_{60} exist in equilibrium with their dimers and that the dimer bond strength depends strongly on the size of the alkyl group R.

$$RC_{60}C_{60}R \rightleftharpoons 2RC_{60}$$

Upon dilution, the ESR signal strength decrease was less than expected for an inert radical and followed the curve (Figure 2) anticipated[14] for the dissociation of a dimer. On the assumption of a small degree of dissociation, the enthalpy change for the above equilibrium, and therefore the dimer bond strength, can be obtained from the slope of the van't Hoff plot in which ln (T × intensity) is plotted against $1000/T$ (Figure 1).[15]

The estimated bond strengths (Table I) of the dimers show a correlation with the size of R, which suggests that bonding in the dimer is greatly influenced by steric effects. This, in turn, strongly suggests that the constituents of the dimer bind at a carbon close to that bearing the substituent R, i.e., head-to-head, rather than head-to-tail as in the Gomberg radical dimer.[13] In such an arrangement, the near equality of the bond strengths for the *tert*-butyl and 1-adamantyl dimers would be expected from the similar steric constraints near the point of attachment. These observations support our conclusion[8] that the unpaired electron in RC_{60} radicals is essentially confined to the three carbon atoms ortho and the two carbon atoms para to the point of attachment of R, namely, Cl, C3, C3′, C5, and C5′. The resulting radical structure, having C_s symmetry, closely resembles two fused cyclohexadienyls:



Molecular graphics calculations[16] show that steric hindrance prevents the dimerization of *tert*-butyl–C_{60} at C1, C5, or C5′, but indicate that dimerization at C3 or C3′ is feasible (Figure 3).

Our failure to detect ESR spectra from the reaction of small radicals (R = H, F, CH_3) with C_{60} is presumably due to the unhindered access of secondary radicals to the spin-bearing carbons of the adduct. It could also be argued that the dimers of such radicals are so thermally stable that the equilibrium is overwhelmingly in favor of the dimer in the accessible temperature range.

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(13) McBride, J. M. *Tetrahedron* **1974**, *30*, 2009.

(14) $[r] = 0.5(0.25K^2 + 4K[d])^{0.5} - 0.25K$, where [r] and [d] are the radical and undissociated dimer concentrations, respectively, and K is the equilibrium constant. ESR signal intensities were adjusted to give the required slope of 2 at zero concentration.

(15) Plotting ln (intensity × T) instead of simply ln (intensity) corrects for loss of signal due to the change in the Boltzmann distribution. "Intensity" means $(\Delta B)^2\ell$, where ΔB is the maximum-slope line width and ℓ is the amplitude of the first-derivative presentation of the signal.

(16) Insight II Molecular Modelling Software, Biosym Technologies Inc., San Diego, CA 92121.

Supramolecular Aggregation of an (η^2-C_{60}) Iridium Complex Involving Phenyl Chelation of the Fullerene

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The past 18 months have seen extraordinary interest in the chemical and physical properties of C_{60} and the higher fullerenes.[1,2] Samples of the fullerenes suitable for X-ray diffraction studies have been difficult to obtain due to poor crystal quality and orientational disorder.[3–6] However, organometallic derivatives in which a metal complex is bonded to the outer surface of the fullerenes have produced crystalline samples of good quality.[7–11] These have demonstrated preferential reactivity of the 6:6 ring fusions in both C_{60}[7–9,11] and C_{70}.[10] Not unexpectedly, the packing of these fullerenes and their derivatives produces cavities within the solid that can be occupied by occluded molecules. Cocrystallization of C_{60} or C_{70} with pentane causes a modification of their crystal structures in order to accommodate solvent occlusion.[12] Additionally, (η^2-C_{60})Ir(CO)Cl$(PPh_3)_2$ crystallizes with five molecules of benzene,[9] (η^2-C_{70})Ir(CO)Cl$(PPh_3)_2$ with 2.5 molecules of benzene,[10] $C_{60}O_2OsO_2$(4-*tert*-butylpyridine) with 2.5 molecules of toluene,[7] and (η^2-C_{60})Pt$(PPh_3)_2$ with a molecule of tetrahydrofuran.[8] In those structures, both intra- and intermolecular interactions of aromatic rings with the fullerenes occur. These are provided by one pair of phenyl rings bonded to the phosphines and, for example, by a benzene of the (η^2-C_{70})Ir(CO)Cl$(PPh_3)_2$ structure which is squeezed between the sides of two adjacent C_{70} moieties.

These observations suggest that it might be possible to construct molecules that provide a host (a molecular egg crate) into which C_{60} (and other fullerenes) might nest. To explore this idea we

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(1) *Fullerenes: Synthesis, Properties and Chemistry of Large Carbon Clusters*; Hammond, G. S., Kuck, V. J., Eds.; ACS Symposium Series 481; American Chemical Society: Washington, DC, 1992.

(2) The entire March 1992 issue of *Accounts of Chemical Research* is devoted to fullerene chemistry.

(3) Heiney, P. A.; Fisher, J. E.; McGhie, A. R.; Romanow, W. J.; Denenstein, A. M.; McCauley, J. P.; Smith, A. B.; Cox, D. E. *Phys. Rev. Lett.* **1991**, *66*, 2911.

(4) David, W. I. F.; Ibberson, R. M.; Matthewman, J. C.; Prassides, K.; Dennis, T. J. S.; Hare, J. P.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *Nature* **1991**, *353*, 147.

(5) Li, F.; Ramage, D.; Lannin, J. S.; Conceicao, J. *Phys. Rev. B* **1991**, *44*, 13167.

(6) Liu, S.; Lu, Y.-J.; Kappes, M. M.; Ibers, J. A. *Science* **1991**, *254*, 408.

(7) Hawkins, J. M.; Meyer, A.; Lewis, T. A.; Loren, S.; Hollander, F. J. *Science* **1991**, *252*, 312.

(8) Fagan, P. J.; Calabrese, J. C.; Malone, B. *Science* **1991**, *252*, 1160.

(9) Balch, A. L.; Catalano, V. J.; Lee, J. W. *Inorg. Chem.* **1991**, *21*, 3981.

(10) Balch, A. L.; Catalano, V. J.; Lee, J. W.; Olmstead, M. M.; Parkin, S. R. *J. Am. Chem. Soc.* **1991**, *113*, 8953.

(11) Fagan, P. J.; Calabrese, J. C.; Malone, B. *J. Am. Chem. Soc.* **1991**, *113*, 9408.

(12) Fleming, R. M.; Kortan, A. R.; Hessen, B.; Siegrist, T.; Thiel, F. A.; Marsh, P.; Haddon, R. C.; Tycko, R.; Dabbagh, G.; Kaplan, M. L.; Mujsce, A. M. *Phys. Rev. B* **1991**, *44*, 888.

0002-7863/92/1514-5455$03.00/0