Figure 2. Plot of log k_q vs ΔG_{et}, see Table I and text. The solid line was calculated from the equation of Rehm and Weller.[18]

agrees well with that observed by Sension et al.,[28] who also reported photochemical reduction of C_{60} by N,N-dimethylaniline. The lifetime of the signal is approximately 50 μs, the same lifetime observed for N,N-dimethylaniline radical cation under the same conditions.

Wudl et al. have shown that C_{60} reacts chemically with primary amines,[32] giving various substitution products. Sension et al.[28] and Wang[33] have shown that the fullerenes form charge-transfer complexes with N,N-dimethylaniline and N,N-diethylaniline, respectively. Figure 1 was obtained by excitation of C_{60} (presumably both complexed and uncomplexed) in the presence of excess N,N-dimethylaniline, under argon. There was no noticeable change in the visible absorption spectrum of C_{60} at the low amine concentrations used during the quenching studies. However, solutions containing excess triethylamine and tripropylamine showed decreases in the C_{60} absorption between 450 and 700 nm, and then new maxima below 450 nm formed after extended laser excitation.

The free energy for electron transfer to $^3C_{60}$ (ΔG_{et}) is calculated from eq 2:

$$\Delta G_{et} = 23.06[E(D^+/D) - E(A^-/A) - \Delta E_{0,0} - e_0^2/a\epsilon] \quad (2)$$

where $E(D^+/D)$ is the oxidation potential of the donor (D, Table I), $E(A^-/A)$ is the reduction potential of the acceptor (A, C_{60}),[34] $\Delta E_{0,0}$ is the excitation energy of $^3C_{60}$, and $e_0^2/a\epsilon$ is the energy gained in bringing the two radical ions to the encounter distance (a) in a solvent of dielectric constant ϵ, where e_0 is the electronic charge.[18,35] In benzonitrile, $\epsilon = 25.2$.[36]

A plot of log k_q vs ΔG_{et} (Figure 2) gives a fairly good correlation with rate constants calculated for electron transfer using the semiempirical Weller equation[18] (solid line). The general shape of the plot is similar to the shape of the calculated line, which assumes a diffusion rate constant of 2×10^{10} M^{-1} s^{-1} in acetonitrile.

However, benzonitrile is 3.6 times more viscous than acetonitrile at room temperature,[36] and the diffusion rate in benzonitrile calculated from the Stokes–Einstein equation should be $\sim5.6 \times 10^9$ M^{-1} s^{-1}, in excellent agreement with the maximum rate constants in Table I.[37]

In conclusion, $^3C_{60}$ is a powerful electron acceptor, with a reduction potential near 1.14 V vs SCE. It is reduced by electron donors according to the Weller equation with the formation of aromatic amine radical cations and C_{60} radical anion, which absorbs between 900 and 1120 nm. Further studies of fullerene excited-state redox behavior are in progress.

(37) A more thorough discussion of solvent effects on electron transfer is in refs 47 and 48 and references therein.

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Self-Assembling Hexameric Helical Bundle Forming Peptides

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Amphiphilic peptides may fold themselves into well-defined secondary structures.[1] DeGrado and other scientists have shown that association of hydrophobic side chains in amphiphilic peptides may lead to the formation of a 4-helical bundle in their 3-dimensional structures.[2-4] Although synthetic 6-helical-bundle peptides have been a subject of current interest,[5] their structures

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(34) Ferrocene/ferrocenium ion standard is more easily reduced in benzonitrile ($E_1 = 0.50$ V) than in CH_3CN (0.41 V).[46] The reduction potential of C_{60} (−0.42 V vs SCE[14,46]) was corrected to CH_3CN from benzonitrile using this difference (−0.09 V) to give −0.51 V vs SCE, the value used to calculate the values for ΔG_{et} given in Table I.

(35) The value for $e_0^2/a\epsilon$ in acetonitrile (0.06 eV[18]), corrected by the ratio of the dielectric constants,[36] is 0.085 eV. Adding this value to −0.51 V for C_{60} gives −0.42 V.[14,34] Since $\Delta E_{0,0} = 1.56$ eV,[1,3,5,10] the reduction potential of $^3C_{60}$ in benzonitrile is 1.14 V vs SCE.

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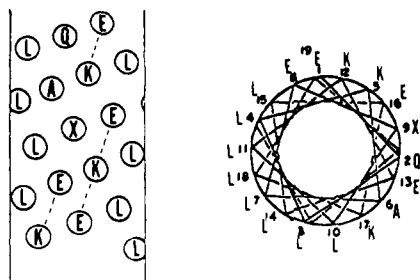
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Communications to the Editor

Figure 1. Octadecapeptide EQLLKALEXLLKELLEKL, peptide F (X = F), and peptide W (X = W) given in the form of a helical-net diagram and an Edmundson circle. Dashed lines indicate stabilizing salt bridges.[15]

have not been demonstrated conclusively in chemical literature.[6] This communication deals with a study of two amphiphilic octadecapeptides, F and W, which self-associate to form a helical hexamer in solution. Peptide F forms an inclusion complex with probe **1** in an aqueous buffer, demonstrating that it contains a hydrophobic cavity. On the basis of the design of our peptides and probe, the results suggest that the helical bundle is twisted, leading to the formation of a cavity with a constricted middle.

In connection with our interest in the spectroscopy of peptides,[7] peptides F and W were synthesized using the conventional method of solid-phase peptide synthesis.[8] These peptides contain eight leucines in the hydrophobic phase (Figure 1) and may have a wider area in the hydrophobic phase for helical association than those forming 4-helical bundles, which often contain only six leucyl groups per helix.[4]

The structures of these peptides were characterized by the following experiments. (a) Their peptide compositions were verified by amino acid analysis. (b) Their apparent molecular weights in phosphate buffer (pH 7.4) were determined by size exclusion chromatography using a Sephadex G-50F column. The results indicate the presence of a single associated form with a degree of aggregation of 5.85–5.86. (c) They display typical CD spectra of α-helical peptides in the phosphate buffer. Their CD spectra were concentration dependent. When their molar ellipticities at 222 nm at concentrations ranging from 3 (monomer) to 200 μM (oligomer) were analyzed according to a known method,[2] it became evident that the data fit well for a hexamer. The results also suggest a free energy of association of about −35 kcal/mol to form the hexamer for both peptides. (d) Peptide W displays a fluorescence maximum at 350 nm which is concentration independent, suggesting that the W group faces the aqueous solvent in the helical bundle.[9]

Peptide F in the phosphate buffer is capable of solubilizing both elaidic acid and terphenyl. However, the solubilization was a metastable phenomenon lasting only several hours, after which these molecules gradually precipitated out of the solution. In order to probe further into the interaction between F and organic substrates, two quaternary ammonium probes, **1** and **2**, containing both segments of aliphatic chains and an aromatic ring, were synthesized. The major difference in their structures is the
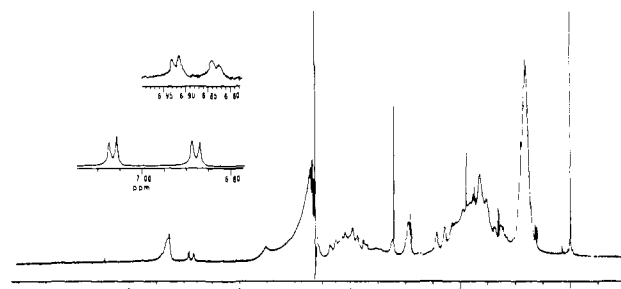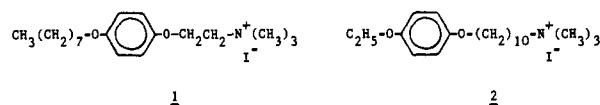
Figure 2. ^{1}H NMR (500 MHz) spectrum of the molecular complex of peptide F and **1**. Insets are the Ar–*H* resonance of **1** in the presence (upper) and in the absence of (lower) of peptide F. The broad signal at δ 4.68 ppm is due to HOD and its suppression, and the sharp signal at δ 3.3 ppm is due to the N$^+$(C*H*$_3$)$_3$ group of **1**.

distance between the polar ammonium group and the bulky aromatic ring. The interaction between F (300 μM) and the probes (50 μM) in deuterated phosphate buffer was investigated using ^{1}H NMR spectroscopy. The signals of Ar–H of **1** (δ 6.88 and 7.07 ppm, J = 10 Hz) broaden and shift upfield in the presence of F (δ 6.83 and 6.92 ppm, J = 10 Hz, Figure 2). The interaction between F and **1** was further investigated with a nuclear Overhauser effect (NOE) experiment. Irradiation of the leucyl methyl proton of F at δ 0.9 ppm leads to a negative NOE on the Ar–H of **1**.[10] The results suggest that an association takes between the aromatic ring of **1** and the leucyl hydrophobic cavity of the hexameric F. On the other hand, the presence of F has no measurable effect on the NMR spectrum of **2**, indicating that no interaction takes between them. The failure of **2** to interact with the hexameric F suggests that the binding cavity of F is not cylindrical, which would have bound both **1** and **2** with equal facility, but has a constricted middle which excludes **2** and its bulky aromatic ring from the cavity. The constriction may be the result of knob-hole or ridge-groove types of interhelical interactions in the oligomer, which lead to the formation of a twisted helical bundle.[11]

Our results suggest that amphiphilic peptides containing an appropriate proportion of hydrophobic to hydrophilic amino acids may self-associate to form a twisted hexameric helical bundle with a cavity of constricted middle. The NMR spectrum of **1** in the presence of F indicates that the dissociation constant of their molecular complex is on the order of micromolarity, which is substantially lower than the K_m of binding of substrates to many model enzymes.[12,13] The generality of our observation and its possible application to the construction of model enzymes[12] and membrane proteins[14] will be explored.

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