Chiral HPLC analysis was performed by using a Diacel Chiralpack AD, hexane/2-propanol (85:15), 1.5 mL/min, 8.72 min ((R)-27), 12.2 min ((S)-27).

Although carbamate-derived Burgess-type salts should be quite stable, the corresponding amide-based compounds are unlikely to be readily isolated; for efforts to use such reagents in synthesis, see ref. [7c] and H. Vorbruggen, K. Krolikiewicz, Tetrahedron Lett. 1994, 35, 7615–7618; c) C. H. Senanayake, F. E. Roberts, L. M. M. Verheooven, P. J. Reider, Tetrahedron Lett. 1995, 36, 2939–2966.


The chiral integrity of products that result from ring opening of the chiral sulfamate by water under acidic conditions followed by neutralization with aqueous sodium bicarbonate has already been verified on a substrate far more prone to racemization (see: ref. [9k]).


Although 1 is available from several commercial sources at prices ranging from US$36–45 per gram, the material is easily synthesized during the course of an afternoon in multigram quantities at a price of less than US$1 per gram by following the procedure described in ref. [7c].


A Supramolecular Array of Fullerenes by Quadrapole Hydrogen Bonding


The chiral integrity of products that result from ring opening of the chiral sulfamate by water under acidic conditions followed by neutralization with aqueous sodium bicarbonate has already been verified on a substrate far more prone to racemization (see: ref. [9k]).
carboxylic acid 4 was converted into acid chloride 5, after which reaction with sodium azide yielded acyl azide 6. Heating 6 in the presence of 6-tridecylisocytosine at 100 °C overnight afforded 8 in good yield (43%), four steps, starting from 4) via bisisocyanate 7. Full experimental details are in the Supporting Information.

The 1H NMR spectrum of a relatively concentrated (100 mM) sample of remarkably soluble (oligo and polymeric) target compound 8 in CDCl3 showed the typical resonances for the six (polymeric) hydrogen-bonding protons at δ = 12.87 (intramolecular, 2H) and at δ = 11.63 and δ = 10.65 (intermolecular, 4H) as well as at δ = 5.72 for the vinylic proton (2H) (Figure 1a). Disrupting all 8-to-8 hydrogen bonding by the addition of a small amount of [D6]trifluoroacetic acid (TFA) resulted in converging of all the resonances from the hydrogen-bonding protons at δ = 11.33. The hydrogen-bonded array can be fully restored, as witnessed by the recovery of the original NMR spectrum by precipitation of the TFA-disrupted polymer with methanol, drying, and subsequent dissolving in CDCl3.

The dynamic behavior of the supramolecular polymer was investigated by 1H NMR spectroscopy by lowering the concentration to 10 mM in CDCl3 (Figure 1b). In addition to all the resonances corresponding to the hydrogen-bonded and vinylic protons observed at 100 mM, new sets of multiple signals appeared. This behavior can be explained by the existence of oligo- and polymeric aggregates in the concentrated solution and a mixture of polymeric and low molecular weight cyclic aggregates in the diluted solution, and is in full agreement with earlier results on supramolecular polymers held together by this coupling unit.9, 10, 12 Theoretically, based on an association constant of 6 × 10^7 M^-1 in CHCl3,9 the population of associates of ultra pure 8 at 100 mM is expected to peak at a M_n of ≈ 3.6 × 10^6. In reality, however, the effect of tiny amounts of (monofunctional) impurities substantially lowering the dynamic molecular weight distribution has to be taken into account.

Further support for the polymeric nature of 8 at high concentration was obtained upon investigating the processability and thin-film behavior of 8: When a filtered solution of 8 (10 mM in CHCl3) was spin-coated on a glass

---

Scheme 1. Synthesis of methanofullerene 8. a) p-TsNHNH2, EtOH, overnight, Δ, 85%; b) NaOMe, py, 30 min, RT; then CO2 in ODCB, 80 °C, 16 h; c) ODCB, 500 W flood lamp, RT, overnight, 49% (b,c); d) ODCB, AcOH, HCl, H2O, overnight, 83%; e) SOCl2, 1 h; f + g) NaN3, ODCB, Me2NCOMe, 75 °C, 30 min; h) 2-amino-4-hydroxy-6-tridecylpyrimidine, py, 100 °C, overnight, 43% (e – h); Ts = tosyl, py = pyridene, Ac = acetyl.

Figure 1. 1H NMR spectra of compound 8 in CDCl3 at different concentrations, a) 100 mM and b) 10 mM.
substrate, a macroscopically homogeneous film was obtained in contrast to the behavior of many low molecular weight fullerene materials. Upon spin-coating, the concentration of 8 increases dramatically, instantly generating higher molecular weight polymer. The UV/Vis spectrum of the film showed substantial scattering, but subtraction of a weighted 1/2 curve regenerated the solution spectrum, albeit somewhat red shifted in the 500–550 nm region. This behavior resembles that of C₆₀ in solution and solid-state spectra.[13]

The 13C NMR spectrum of polymeric 8 (at 100 mT in CDCl₃) showed 15 signals for the fullerene core in accordance with a C₆₀ symmetry for the monomer. Additional resonances at δ = 172.87, 156.63, 154.10, and 152.33, which correspond to the 2-ureido-4-pyrimidinone moiety, and at δ = 78.21 and 39.92, diagnostic for the cyclopropyl moiety, were observed. The UV/Vis of 8 revealed the characteristic absorptions for a methanofullerene. There were no significant spectral shifts in the 400–750 nm region upon varying the concentration between 0.01 and 4 mM, which indicates little or no ground-state interfullerene interaction in the “supra polymer”. The FT infrared (IR) spectrum of 8 (KBr pellet) showed the typical peak pattern for a 4[H]-ureido-4-pyrimidinone derivative (1697, 1656, 1585, 1524 cm⁻¹) together with a peak at 526 cm⁻¹, diagnostic for a (monomethano)fullerene. Finally, in the matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrum of 8 a parent peak at m/z 1457.79 was detected, which corresponds to the monomer formula. No higher aggregates were observed.

The redox behavior of 8 (at 0.3 mM in ODCB:MeCN 4:1) was studied by cyclic voltammetry (Figure 2). Four quasi-reversible fullerene-core reduction waves were observed, with values typical for this type of methanofullerene.[7] A small wave at −1.79 V, which corresponds to the reduction of the ureidopyrimidinone moiety was also observed. In the dimer, this moiety showed two reduction waves at −1.15 (sh) and −1.84 V.[7] In 8 only the latter can be distinguished, probably because of overlapping of the first with the second reduction wave of the fullerene moiety, as indicated by the increased size of the 2nd reduction wave, compared to the first. The presence of a clean set of waves indicates that there is little or no interaction between the fullerene cages, in agreement with the redox behavior determined for the corresponding supramolecular dimers (Figure 2).[7]

Polymer 8 is first example of a hydrogen-bonded fullerene array. In the highly dynamic polymeric state, the chemical integrity of the monomeric moiety is fully preserved, also with respect to its redox and UV/Vis behavior. Application in supramolecular electronics, for example, in combination with (supra)molecular donor materials, is now underway.

Received: July 30, 2001
Revised: December 12, 2001 [Z17633]