$M_\odot$ per year) and by the internal adjustment from the assumed initial configuration toward equilibrium. The main energy sink is radiation lost to the cold (10 K) molecular cloud envelope. The thermal profiles are consistent with an independent calculation (*16*) based on plane parallel radiative transfer in a viscous accretion disk undergoing mass accretion at the rates used in these models (*12*). The profiles are also similar to those derived by use of this same numerical technique to model an α accretion disk with $\alpha \sim 0.01$ and the same mass accretion rates (*12*).

These models demonstrate that the ice condensation radius does not move inward very rapidly as the stellar mass is decreased, which is contrary to the result for the free-space temperature profile. This is because the disk temperature profiles in these models are largely determined by the disk properties (disk masses were assumed to be constant) and hence are somewhat decoupled from the stellar masses. Jupiter-like planets are thus likely to be found orbiting low-mass stars at distances not much different (~4 to ~6 AU) than those in our solar system. This result improves the chances that the first extrasolar planet around a low-mass star will be detected by astrometry or direct detection but decreases the likelihood that the first extrasolar planet will be found by Doppler spectroscopy or photometry (*9*).

If extrasolar Jupiter-like planets generally are formed around 5 AU, then their orbital periods will vary with stellar mass as $P \propto M_s^{-1/2}$; that is, the periods will increase with decreasing stellar mass, which again is contrary to previous expectations (*9*). Extrasolar planet searches would then require even longer time intervals than are currently envisioned in order to follow the system for an orbital period. Finally, if extrasolar Jupiter-like planets are found at these distances from low-mass stars, such discoveries would strengthen our confidence in the general theoretical description of protoplanetary disks.

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Synthesis of Linear Acetylenic Carbon: The "*sp*" Carbon Allotrope

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A carbon allotrope based on "*sp*" hybridization containing alternating triple and single bonds (an acetylenic or linear carbon allotrope) has been prepared. Studies of small (8 to 28 carbon atoms) acetylenic carbon model compounds show that such species are quite stable (130° to 140°C) provided that nonreactive terminal groups or end caps (such as tert-butyl or trifluoromethyl) are present to stabilize these molecules against further reactions. In the presence of end capping groups, laser-based synthetic techniques similar to those normally used to generate fullerenes, produce thermally stable acetylenic carbon species capped with trifluoromethyl or nitrile groups with chain lengths in excess of 300 carbon atoms. Under these conditions, only a negligible quantity of fullerenes is produced. Acetylenic carbon compounds are not particularly moisture or oxygen sensitive but are moderately light sensitive.

The known allotropes of carbon are based either on sp^3 hybridization of carbon (diamond) or sp^2 hybridization (graphite, fullerenes, and nanotubes). Although Hoffman (*1*) had predicted in the 1960s that other allotropes of carbon would be synthesized, the generally held view was that the acetylenic carbon allotrope was unstable. In this report, we present evidence for the synthesis of a carbon allotrope based on "*sp*" hybridization that contains alternating triple and single bonds (an acetylenic or linear carbon allotrope) (*2–7*). Studies of acetylenic model compounds (following or modifying reported syntheses and through new synthetic routes) suggested the crucial role of nonreactive terminal groups, or end-caps, for stabilizing these molecules against further reactions. Also, previous work on the gas-phase synthesis of carbon clusters has been reinterpreted and reproduced and we have shown that these methods can produce a substantial fraction of acetylenic carbon gas-phase species. We show that the gas-phase synthetic conditions normally used to generate fullerenes can be used to produce long-chain acetylenic species. When end-capping groups are present, acetylenic carbon is produced at the expense of fullerene synthesis, which depending on conditions is either totally eliminated or substantially suppressed.

The synthesis of mixtures of long-chain acetylenic carbon species [(α-ω-bis(triethylsilyl)polyynes up to 32 carbon atoms] with alternating single and triple bonds was reported by Walton and co-workers in 1972 (*8*). They had prepared, using copper chloride (Hay coupling), mixtures of acetylenic carbon compounds that contained 2 to 16 acetylene units (Et, ethyl):

$$(\mathrm{Et})_3\mathrm{Si{-}(C{\equiv}C)}_n\mathrm{{-}Si(Et)}_3$$

$$n = 2 \text{ to } 16$$

Walton proposed that the bulky triethylsilyl groups were useful end groups for stabilizing

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the compounds by keeping the chains apart in solution or in the gas phase where they could not collide and polymerize. [In order to effectively prevent chain collisions in solution or the gas phase, all molecules would have to be oriented in a one-dimensional (linear) manner.]

Although our studies have led to the conclusion that acetylenic carbon chains terminated with delocalized electrons (rather than end groups) are extremely unstable (9) and that hydrogen-capped polyynes are normally stable only below room temperature, we have found (see below) that groups bulkier than hydrogen stabilize acetylenic carbon compounds mechanistically. There are a number of rearrangement mechanisms which are possible with hydrogen transfer that are not accomplished easily with bulky alkyl or aryl groups. Walton and co-workers found that their lower molecular weight triethylsilyl compounds were stable at room temperature in solution and some would even pass through a gas chromatograph. As primary evidence for the longer chain species were a succession of peaks in their ultraviolet (UV) spectra that they believed correlated with increasing alkyne conjugation. For C_{32}, they reported that significantly less than 0.5% of the mixture of compounds produced was of that composition. They also reported that beyond ~C_8 the chains became increasingly less stable as they became longer. Only the lowest members of the series were stable enough to be isolable. Walton and co-workers did not focus on these acetylenic chain compounds with respect to their potential to lead to a new allotrope of carbon. Diederich and co-workers have also reported the synthesis of mass-spectrometric quantities of a C_{18} alkyne-containing carbon ring (*10*) by flash-heating [18]annulene precursors.

We have prepared a number of model compounds with various end-cap groups and have studied these with a number of techniques, including nuclear magnetic resonance (NMR, especially ^{13}C NMR), x-ray diffraction (XRD), infrared (IR) spectroscopy, high-performance liquid chromatography (HPLC), and mass spectrometry (MS). The study of model compounds allowed us to probe the stability of acetylenic carbon species. These compounds also were of interest as precursors for synthesizing longer chains and as structural models for characterizing linear carbon. This work was particularly important for liquid and solid ^{13}C NMR characterization.

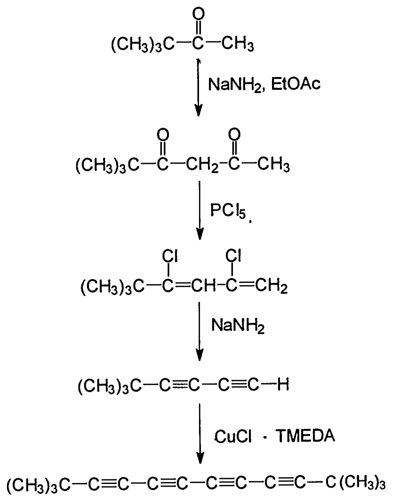
We synthesized (t-Bu)C_8(t-Bu) (t-Bu, *tert*-butyl) through the procedure outlined in Scheme 1. Large amber crystals were obtained that melted at 99°C and were thermally stable to at least 130°C. Between 130° and 140°C, polynuclear hydrocarbons and graphitic materials began to form through polymerization.

The crystal structure of this compound reveals the presence of alternating long and short bonds. The C-7–C-7′ distance is 3.502 (Table 1 and Fig. 1) (±0.002) Å, and thus the carbon chains cross within 3.5 Å of one another without polymerization or cross-linking.

A study of the crystal structures of a number of similar model compounds indicated that there are two primary stacking patterns. One is the crossed chain structure exhibited by this molecule, whereas a number of other species crystallize in a planar brick-like structure in which the capping group stacks in between the chains above and below in an interlocking fashion. Such a crystal structure was observed and reported recently for a C_{10} acetylenic model compound prepared by Diederich and co-workers (*11*).

All of the carbon resonance can be identified in the ^{13}C NMR spectrum of the (t-Bu)C_8(t-Bu) acetylenic model compound (Fig. 2); the resonance at 54 ppm is a solvent peak. The solid-state ^{13}C NMR of this compound is identical to the solution spectrum, except for a peak at 64 ppm that is a lattice interaction.

The (t-Bu)C_8(t-Bu) model compound is stable at pressures up to 60 kbar in a belt apparatus. These compounds do not readily form graphite under pressure. A (t-Bu)C_8(t-Bu) sample that had been loaded to 40 kbar pressure at room temperature for 1 hour showed no changes in its IR spectra, XRD pattern, or physical properties. At 60 kbar, a very small amount of graphitization (~2%)



Scheme 1.

Table 1. X-ray diffraction study of (t-Bu)C_8(t-Bu). Numbering scheme: C atoms 1 to 8 form the main chain; C atoms 9 to 12 [attached to C(8)] and C atoms 13 to 16 (attached to C(1)] form the two t-Bu groups. The crystals (0.2 mm by 0.4 mm by 0.2 mm) belonged to space group *Pbcn* with lattice constants a = 11.185 (7) Å, b = 11.781 (7) Å, c = 22.36 (2) Å for a volume V = 2947 (4) Å^3 (standard errors in last digits in parentheses). The x-ray wavelength was 0.71069 Å and the sinθ/λ limit was 0.48 Å^{-1}. Of 1734 total reflections, 770 were used in the structural analysis [intensity $I > 3\sigma(I)$]. The number of variable parameters was 146, and the final agreement factors were $R(F)$ = 0.057 and $R(wF)$ = 0.073.

Bond distances (Å)		Bond angles (degrees)			
		Main chain		t-Bu groups	
C(13)-C(1)	1.453 (9)	C(13)-C(1)-C(2)	178.8 (6)	C(10)-C(9)-C(8)	110.1 (5)
C(2)-C(1)	1.217 (9)	C(3)-C(2)-C(1)	177.6 (6)	C(11)-C(9)-C(8)	108.9 (5)
C(3)-C(2)	1.377 (9)	C(4)-C(3)-C(2)	178.5 (5)	C(12)-C(9)-C(8)	109.6 (5)
C(4)-C(3)	1.172 (8)	C(5)-C(4)-C(3)	177.4 (6)	C(11)-C(9)-C(10)	109.2 (6)
C(5)-C(4)	1.351 (9)	C(6)-C(5)-C(4)	176.7 (6)	C(12)-C(9)-C(10)	108.6 (6)
C(6)-C(5)	1.218 (9)	C(7)-C(6)-C(5)	178.9 (6)	C(12)-C(9)-C(11)	110.4 (7)
C(7)-C(6)	1.362 (10)	C(8)-C(7)-C(6)	176.1 (6)	C(14)-C(13)-C(1)	108.8 (5)
C(8)-C(7)	1.202 (8)	C(9)-C(8)-C(7)	179.4 (6)	C(15)-C(13)-C(1)	108.5 (5)
C(9)-C(8)	1.446 (9)			C(16)-C(13)-C(1)	107.5 (4)
C(10)-C(9)	1.517 (8)			C(15)-C(13)C(14)	109.7 (5)
C(11)-C(9)	1.500 (8)			C(16)-C(13)C(14)	109.8 (5)
C(12)-C(9)	1.508 (9)			C(16)-C(13)C(15)	112.5 (5)
C(14)-C(13)	1.526 (8)				
C(15)-C(13)	1.522 (8)				
C(16)-C(13)	1.536 (7)				

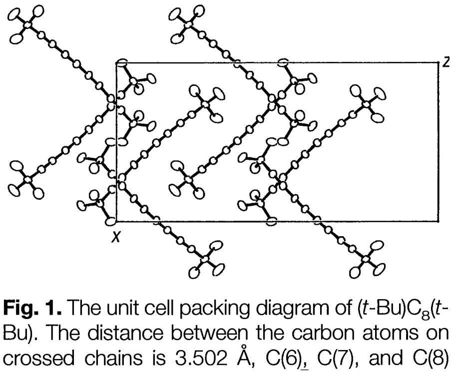


Fig. 1. The unit cell packing diagram of (t-Bu)C_8(t-Bu). The distance between the carbon atoms on crossed chains is 3.502 Å, C(6), C(7), and C(8) have the closest approach nonbonding distances of C(7) . . .C(7)′ = 3.502 Å, C(7) . . .C(8)′ = 3.662 Å, C(6) . . .C(8)′ = 3.755 Å, C(6) . . .C(7) = 3.779 Å, and C(8) . . .C(8)′ = 3.941 Å. These distances are typical of nonbonding π-interactions and are certainly long enough to preclude strong intermolecular bonding interactions.

was observed. We are optimistic that linear carbons with chain lengths much longer than 300 carbon atoms may be synthesized at such high pressures.

A second synthetic approach developed in our laboratory makes use of a reaction described by Viehe (12) in which carbon was produced as a by-product. The condensation reaction of the lithium compound, $Li{-}C{\equiv}C{-}Br$, begins to form carbon chains at −56°C in liquid NH_3. We obtain better results using organic solvents. (Caution: This reaction must be carefully controlled and cooled or the reaction is potentially explosive. All work should be conducted behind explosion shields.)

By modifying this synthesis, we have prepared mixtures of acetylenic-chain carbon compounds capped with phenyls (we have used both phenyllithium and phenylchloride as capping reagents, sometimes in succession) that contain chains of 16, 24, and 28 carbons (Fig. 3). This mixture of compounds does not separate on the types of columns used to separate fullerenes (Al_2O_3) but rather reacts with such columns. Mass spectra of mixtures indicates that phenyl-capped parent ions for C_{16}, C_{24}, and C_{28} peaks are produced. A C_{24} cyclic species may also be present in the mixture. Thermal stability studies on the mixtures show that the compounds in this mixture are also stable to at least 130°C.

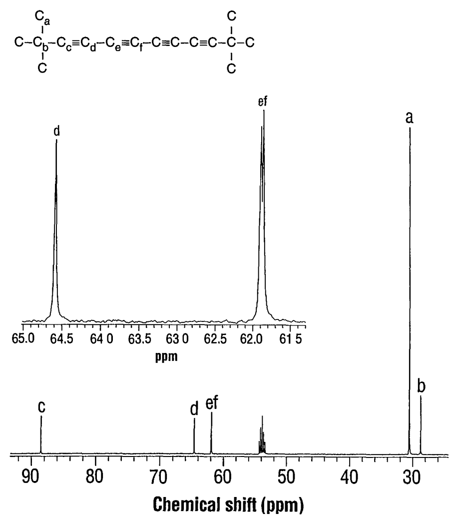


Fig. 2. The ^{13}C solution spectrum of (*t*-Bu)C_8(*t*-Bu) under moderate resolution; inset, high resolution of peaks e and f.

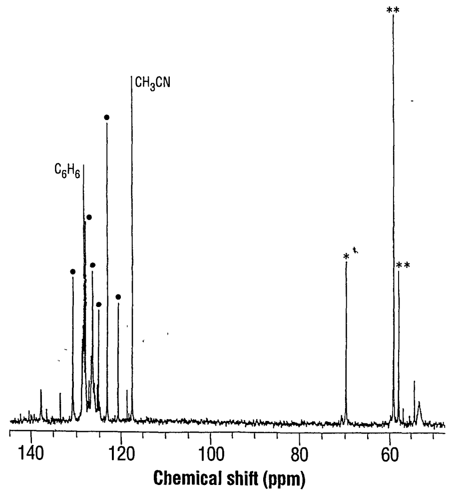


Fig. 3. The ^{13}C NMR of mixture of at least three higher molecular weight phenyl capped acetylenic carbon compounds. Acetylenic carbon peaks are centered at 60 to 70 ppm (*, 69.731, 59.012, 59.049, 57.876, and 57.825 ppm). Phenyl peaks occur at 125 ppm (●, 130.755, 128.122, 126.586, 125.209, 123.146, and 120.659 ppm).

Increasing experimental evidence and a number of observations in our laboratory have led us to believe that the pioneering results reported by Rohlfing, Cox, and Kaldor (13) (see Fig. 4) on the gas-phase syntheses of carbon clusters likely produced some linear carbon chains. The carbon cluster peaks in the spectrum shown in Fig. 4B with a mean carbon cluster size of 116 carbon atoms were likely to be the linear carbon chains that can be stable in the gas phase at high temperatures. Such high-temperature acetylenic chains with delocalized electrons on either end would, upon condensation, polymerize to the "soot" that usually accompanies the synthesis of fullerenes. In view of our previous work on the stability of end-capped model compounds, we set out to design an experiment to test our hypothesis.

Lower molecular weight carbon clusters may be capped in the gas phase (13–15) with end groups such as nitrile $(C{\equiv}N)$, hydrogen, and CH_3. Kaldor *et al.* (13) observed $K{-}(C{\equiv}C)_n{-}K$, $3 \le n \le 12$ when they vaporized graphite presoaked in aqueous KOH with a supersonic He-laser system. We used a laser to vaporize graphite into an apparatus designed with Krätschmer-Huffman dimensions (16), similar mean free paths, and partial gas pressures. Our goal was to cap and thus stabilize these high-temperature linear carbon species with CF_3 radicals (17) and $C{\equiv}N$ radicals. Helium was used as a third body gas.

Graphite was vaporized with a Spectra-Physics 820 1.5-Kw, continuous-wave CO_2 laser into an apparatus shown in Fig. 5 containing a 90% He: 10% C_2N_2 mixture at 0.2 atom of pressure. Multigram quantities of graphite could be vaporized for more than 1 hour.

The vaporized carbon chains react, both in the gas phase and upon condensation on

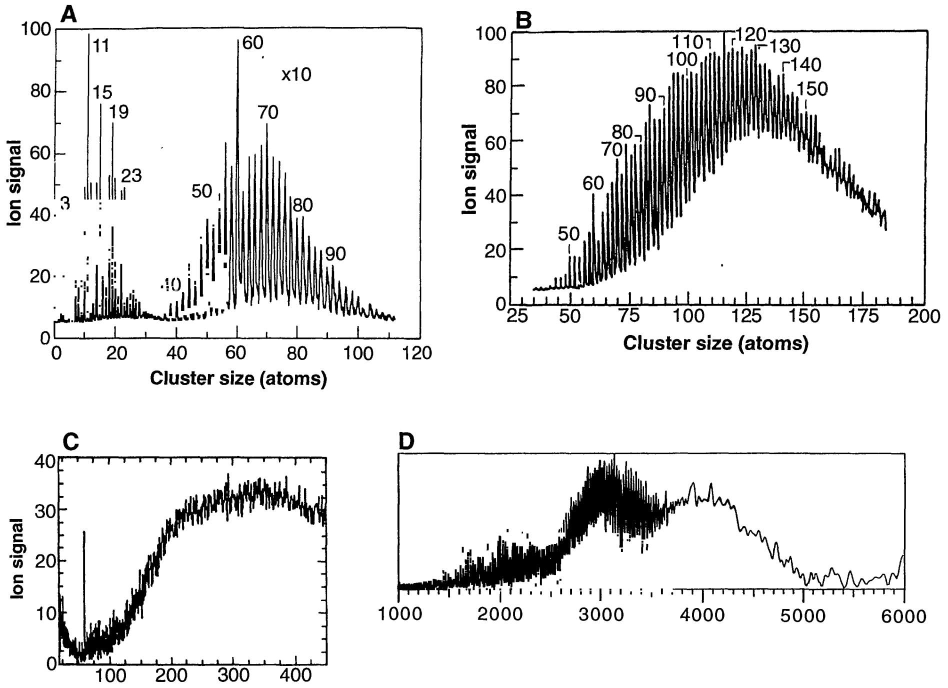


Fig. 4. (**A**) The mass spectra of supersonic carbon cluster beams by Kaldor and co-workers (lower molecular weight region) (*13*). (**B**) The mass spectra of supersonic carbon cluster beams by Kaldor and co-workers (higher molecular weight region) (*13*). Note that the average carbon cluster size is ~116 carbon atoms (*11*). [Reprinted from (*11*) with permission © American Institute of Physics] (**C**) The mass spectrum of carbon clusters produced by Kaldor and co-workers (*18*) using argon as the third body gas. Note that the average carbon cluster size is ~325 carbon clusters. [Reprinted from (*18*) with permission © American Institute of Physics] (**D**) The Fourier-transform mass spectrum of CF_3 capped acetylenic carbon chains produced using argon as a third-body gas. Note that the high-resolution spectrum goes out of resonance at mass 3900; however, species are observed out to mass 5000.

the walls of the glass reactor, with C≡N groups generated by the plasma sheath associated with the laser vaporization of carbon. The reaction apparatus was at room temperature. Initially the reaction products were dissolved in toluene. The walls of the reactor were washed down, and typically about 0.5 to 1 g quantities were obtained in a 1-hour run. The toluene was then analyzed for fullerenes and other species by ^{13}C NMR. A sample of the toluene extract was evacuated to dryness and then redissolved in tetrahydrofuran (THF) to concentrate the acetylenic carbon compounds formed in the reactor and to remove small amounts of fullerenes that may also be produced. The THF was then evaporated under vacuum, and the extracted linear carbon capped species were redissolved in $CDCl_3$ for ^{13}C NMR analysis. A typical ^{13}C NMR spectra shows acetylenic carbon compounds with peaks at 54.265, 54.554, 54.812, and 69.113 ppm (Fig. 6). Normally no fullerenes were present in these toluene extracts, although occasionally a very minor amount of C_{60} and C_{70} was observed. An ms analysis of the length of the acetylenic carbon chains produced in the experiment was performed with a stainless steel probe coated with the solid residue of the THF extract. Mass spectra were taken with Nd:YAG laser desorption with a Fourier-transform (FT) ion cyclotron resonance mass spectrometer with a dual cell ion trapping assembly controlled by a Nicolet 1280 data station that included a 3.0-T superconducting magnet. A typical spectrum observed around mass number 1200 (100 carbon atoms) shown in Fig. 7 exhibits a repetitive carbon (24 amu) pattern. It is difficult (if not impossible) to distinguish the C≡N capping groups on the end of a long nitrile chain even at high resolution from a chain of identical length containing all carbon atoms.

When CF_3 radicals were used as capping agents (*17*), the carbon isotope pattern is still complicated but each carbon cluster becomes more distinct (see Fig. 7C). Although it is apparent from the complexity of the mass spectrum that C≡N capping groups may be in place, even the high-resolution spectra at C_{80} to C_{100} are not definitive. In both the C≡N experiments and the CF_3 experiments, the materials prepared and extracted were amber to dark brown in color both in solution and in the solid (powdered) state. The IR spectra in $CDCl_3$ of the capped acetylenic carbon chains, however, show definitive evidence for nitrile C≡N end groups that appear as a multiplet between 2337 and 2362 cm^{-1}.

In 1988, Kaldor, Cox, and Reichmann (*18*) again vaporized carbon to produce carbon clusters but used argon, a heavier third-body gas (Fig. 4C). They found that clusters of 100 to 450 carbon atoms appear at strictly even mass numbers. Their unattenuated spectrum is based on the absolute ion currents. The "composite mass spectra" of this type show more accurately the relative intensities in the spectrum. The fullerenes, C_{60} and C_{70}, are dwarfed in the spectrum by numerous peaks with a mean carbon cluster size of 300 carbon atoms. Their central conclusion from this spectrum was that C_{60} constituted <0.001 of the ion current.

We believed that these clusters produced by Kaldor *et al.* (*18*) were long acetylenic chain compounds with delocalized electrons on either end. We therefore did a capping experiment with both CF_3 radicals and later with cyanogen designed to produce capped 300 carbon atom chains. To generate CF_3 radicals, C_2F_6 was passed through a 10-MHz radio frequency discharge (*17*) with about 20 W of power applied to produce a very clean mixture of 99% CF_3 radicals and 1% C_2F_5 radicals. The experiment was conducted in a slightly different manner than the cyanogen preparation previously discussed. We know that CF_3 radicals are stable on a glass wall in a condensed form only at temperatures below −78°C. Therefore, in order to obtain benefit of both gas-phase and surface end-capping reactions, we cooled the walls of the glass reactor to −196°C and first condensed a considerable amount of CF_3 radicals on

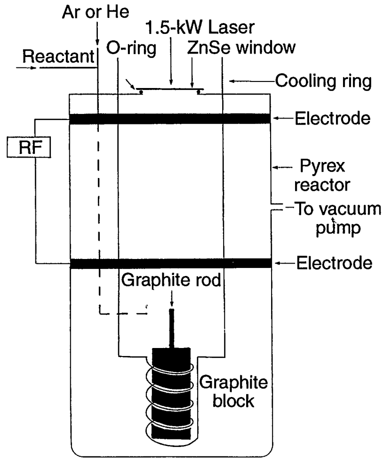


Fig. 5. Apparatus used for syntheses of high molecular weight capped acetylenic carbon chains. The CO_2 laser power in this experiment was 1.3 to 1.5 kW. The apparatus was 19 cm in diameter and 35 cm in height. The electrodes are used only for the C_2F_6 reaction; the dash line for the reactant feed is used only for the cyanogen reaction.

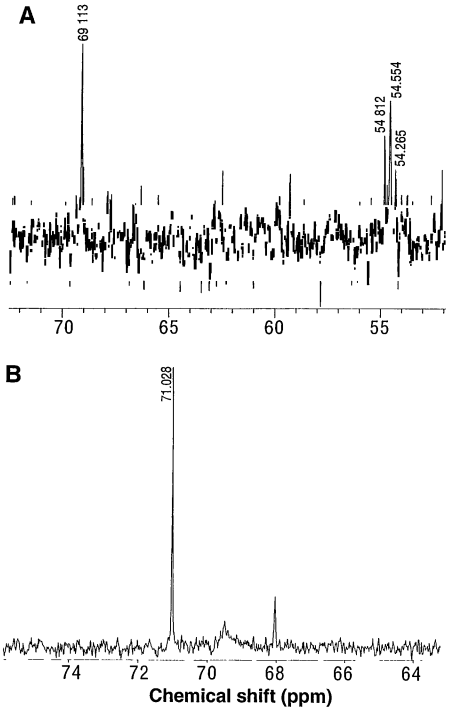


Fig. 6. The ^{13}C NMR spectra in deuteroacetone of (**A**) C≡N and (**B**) CF_3-capped acetylenic carbon chains.

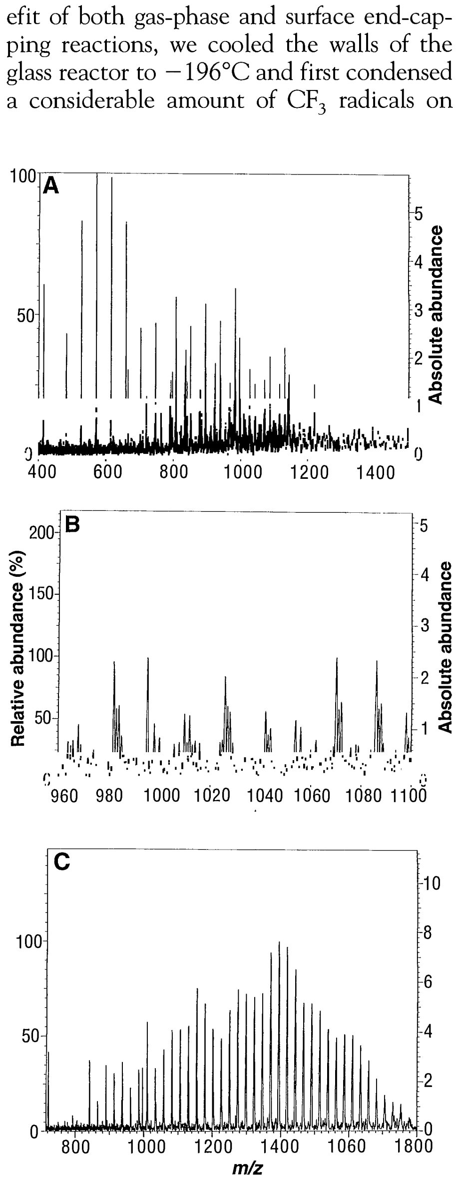


Fig. 7. (**A**) The Fourier-transform high-resolution mass spectrum of C≡N capped acetylenic carbon chains. (**B**) More detailed mass spectrum from mass 960 to mass 1100. (**C**) The Fourier transform mass spectrum of CF_3 end-capped acetylenic chains produced with He as a third body gas.

the walls. We then vaporized the carbon and periodically would turn off the vaporization source to condense more CF_3 radicals on the walls, thus sandwiching the CF_3 radicals between layers of cryogenically cooled carbon clusters. This low-temperature approach may have the effect of stabilizing the carbon chains terminated with delocalized electron end caps. A reaction may also occur between CF_3 radicals and carbon chain ends as the mixture is warmed in addition to the capping reactions that occur in the gas phase. Again in this experiment we worked at $\sim$0.2 atm of argon so that we could expect to be in concert with the results of Kaldor *et al.* (*18*), which produced a mean carbon cluster size of 325 carbon atoms.

Initially the reaction products after warming were dissolved in toluene and then in THF to purify the acetylenic carbon species. The products obtained are amber to dark brown in color. On many runs with the CF_3 capping procedure, there was no detectable fullerene production, whereas on other runs we saw small amounts in the toluene fraction. The THF-extracted sample was then redissolved in deuteroacetone and the ^{13}C NMR spectrum (Fig. 6B) was obtained. The largest peak is centered at 71.0282 ppm from deuteroacetone. No other carbon-containing species were observed from 10 to 200 ppm in the ^{13}C NMR spectrum.

A FTIR spectrum was run on the sample in deuteroacetone and the deuteroacetone bands were then subtracted from the spectrum. A very strong band at 1200 cm^{-1} obscuring some of the $C\equiv C$ bending modes of the linear carbon chain provided definitive evidence of CF_3 substitution. A ^{19}F NMR spectrum in $CDCl_3$ showed a strong sharp signal for CF_3 groups at -54.7 ppm from $CFCl_3$.

Next the THF extract was coated onto a solid probe and the solvent vaporized from the probe. The FT mass spectrometer with the Nd:yttrium-aluminum-garnet laser source was used to obtain spectra as in the previous example. A large envelope with an average molecular weight of 3600 (300 carbon-atom chain) was observed (Fig. 4D) with carbon isotope patterns 24 mass numbers apart.

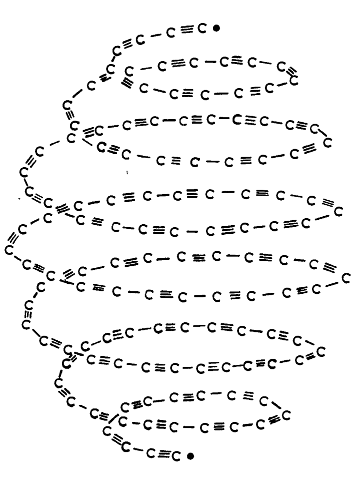


Fig. 8. The spiral zipper hypothesis.

We ran a number of experiments with the same synthetic apparatus and procedures but omitting CF_3 or $C\equiv N$ capping groups. Fullerenes including C_{60} and C_{70} were prevalent in the toluene sample, whereas in the THF sample there were no observable acetylenic species in the ^{13}C NMR spectrum.

We conclude that the formation of fullerenes is suppressed by adding free radicals to cap the ends of chains. Thus when the carbon experiment is set up where there is a significant amount of free radicals, no fullerene structures are produced in isolable quantities in a macroscopic experiment. No acetylenic carbon species could be extracted from the products of typical laser fullerene experiments or Krätschmer-Huffman type experiments; that is, no acetylenic carbon NMR peaks have been observed.

These observations have led us to believe that these acetylenic carbon chains with delocalized electrons on either end are likely to be precursors for formation of fullerenes such as C_{60} and C_{70}. There is a chain curvature in the crystal structure of the model compound (see Table 1). We view the diradical linear carbon chains to frequently exist in spiral-like chain structures as shown in Fig. 8.

We propose that these diradical species, which are unstable at room temperature, are the precursors for fullerenes. When these condense, a certain fraction of the linear chains undergo a series of zipperlike reactions to become fullerenes and others become fullerene "soot."

Bowers and co-workers, studying carbon clusters from $n = 3$ to 60, concluded that "monocyclic rings" and "open fullerene" structures occur based on distinct arrival times from the fullerenes in MS experiments (*19*). Subsequently there has been work by Jarrold and co-workers in which the same species were labeled "polycyclic polyyne ring isomers" (*20*). They studied carbon clusters ranging from 50 to 70 carbon atoms in size and have "annealed" such species in a mass spectrometer to form C_{60} and other fullerenes. We would postulate that our uncapped linear carbon diradical species are the same species as the "open fullerene" and "polycyclic polyyne ring isomer" structures.

We have spent some time questioning whether long end-capped chains of acetylenic carbons constitute a new carbon allotrope. We note that the fullerenes are the only allotropes of carbon known to occur without end groups. They are molecular allotropes. Both diamond and graphite surfaces are terminated with hydrogen, hydroxyl, or oxide end groups (*21*).

It would be preliminary to conclude that the acetylenic carbon species we produce are strictly linear, and we would be surprised if some cross-linked acetylenic carbon species were not present. However, no evidence for cross-linking has been found. In addition to the fact that no spectral observations indicate cross-linking, the properties of the new capped chain materials argue strongly against cross-linking. In contrast to all other forms of carbon, including fullerenes, the capped linear carbon chains are very soluble in most organic solvents, producing rich amber colored solutions at lower molecular weights and concentrated dark brown solutions at carbon chain lengths of about 300. The properties of the solid materials differ very significantly from the cross-linked "fullerene soot" associated with fullerene production. The linear carbon material on the sides of the synthesis reactor have a gossamer-like character and are easily collected off the walls even without the use of solvents, whereas the cross-linked "fullerene soot" is difficult to scrape off the glass walls of the reactor. In contrast, "fullerene soot" is only slightly soluble in toluene and is insoluble in most organic solvents. Based on some empirical considerations and considerable experience in the area, we would estimate that of the ion current (Fig. 4C) in which Kaldor *et al.* (*18*) observed a large envelope of clusters from 100 carbons to 450 carbons, at least two-thirds of the ion current is due to linear carbon species.

A discussion of applications of such linear carbon species, which we are rather certain stable species will be prepared of even higher molecular weight, is also preliminary. However, we observe that these carbon species would have electron density higher than any allotrope of carbon (graphite) or any known organic compound and are likely to be better conductors than known carbon-containing species. The high degree of solubility of linear carbon in organic solvents is a novel feature for any form of carbon and should lead to many technological applications, including carbon coatings, possibly one activated by UV light. Further, because this allotrope is decidedly less stable than either graphite or diamond, it should be under appropriate conditions an excellent precursor for diamond synthesis as well as for graphite coating. Certainly linear carbon will have an extensive reaction chemistry; it is more reactive than the three existing allotropes of carbon and will perhaps prove to be the most reactive solid form of carbon. Linear carbon can function as a zero hydrogen fuel and could be useful in fuel cells based on oxygen combustion. We believe that most organic end groups and perhaps many inorganic end groups will stabilize linear carbon.

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Visualization of Surfactants on Nanostructured Palladium Clusters by a Combination of STM and High-Resolution TEM

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Scanning tunneling microscopy (STM) and high-resolution transmission electron microscopy (TEM) have been used to determine the dimensions of a series of palladium clusters stabilized by tetraalkylammonium salts. Electrochemically prepared colloids were used in which the average diameter of the inner metal core was varied between 2 and 4 nanometers, and the size of the ammonium ions was adjusted in the series $^+N(n\text{-}C_4H_9)_4 < {}^+N(n\text{-}C_8H_{17})_4 < {}^+N(n\text{-}C_{18}H_{37})_4$. The difference between the mean diameter determined by STM and that measured by TEM allows the determination of the thickness of the protective surfactant layer. On the basis of these studies, a model of the geometric properties of ammonium-stabilized palladium clusters has been proposed. Suggestions for the mechanism of the STM imaging process are also made.

Current interest in metal clusters and colloids in the size range of 1 to 10 nm is increasing because of their actual and potential use as catalysts and as advanced materials in electronics (*1*). In order to prevent agglommeration with the formation of large particles or powders, these nanostructured clusters usually need to be protected by stabilizers such as polymers (for example, polyvinylpyrrolidone) (*2*), ligands (for example, phenanthroline) (*3*), or surfactants (for example, tetraalkylammonium salts) (*4*). Synthetic routes include metal vaporization and chemical reduction of metals salts in the presence of the stabilizers (*1–4*). In most cases, the nature of stabilization is not well understood (*5*), and knowledge of the actual structure and dimensions of the materials is limited. Generally, high-resolution transmission electron microscopy (TEM) has been used, but this technique provides only information regarding the size of the metal cores (*6*). Because scanning tunneling microscopy (STM) is a powerful tool for the characterization of surfaces and catalysts (*7*), it might be expected to be useful in the determination of the outer dimensions of the actual colloidal materials. The difference between the mean diameter determined by each of these methods, d_{STM} and d_{TEM}, would be 2*S*, where *S* is the thickness of the protective layer (Fig. 1). Previous STM studies of gold and Pd clusters stabilized by phenanthroline derivatives have culminated in the gross characterization of the surface topography, but so far, details regarding d_{STM} have not been possible (*8*).

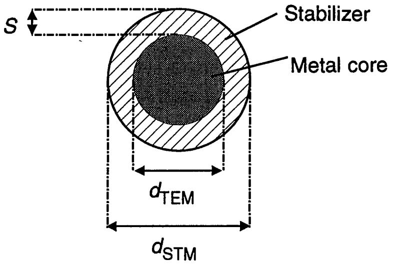

Fig. 1. Schematic diagram defining the terms used in this study.

We have recently described the size-selective electrochemical synthesis of tetraalkylammonium-stabilized Pd and Ni clusters: Control of particle size (d_{TEM}) is possible by simple adjustment of the current density (*9*). Because the bulkiness of tetraalkylammonium ions $^+NR_4$ can be varied by the proper choice of R groups, we have a simple experimental method for the systematic preparation of ammonium-stabilized clusters in which the geometric parameters (Fig. 1) can be varied at will. In this report, we present the results of a study combining STM and high-resolution TEM of stabilized metal clusters. Direct measurements of d_{STM} and d_{TEM} for a series of tetraalkylammonium-stabilized Pd clusters is provided, allowing a fairly detailed study of the interaction between tetraalkylammonium ions and metal clusters.

A series of Pd clusters was synthesized as previously described (*9*). We prepared the samples for the TEM studies by dip coating a commercially available TEM grid (400 mesh, copper with 5-nm amorphous carbon) with ~10^{-4} M solutions of the colloids. The images were taken at a magnification of 3 × 10^5 with a Hitachi HF2000 high-resolution TEM at an acceleration voltage of 200 keV. Materials with different d_{TEM} values but with the ammonium salt remaining the same were investigated, along with materials in which the d_{TEM} values were approximately constant but the size of ammonium ions varied (Table 1). The clusters were then studied by STM. Substrates for the STM measurements were quartz slides with vapor-deposited gold films 200 nm thick. An essential step necessary

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