Synthesis of Linear Acetylenic Carbon; The Fourth Carbon Allotrope

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A new carbon allotrope based "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 (130-140°C) provided that nonreactive terminal groups or end caps, such as t-butyl, triethylsilyl, phenyl, trifluoromethyl, or nitrile groups, are present to stabilize these molecules against further reactions. Using laser based synthetic techniques in the presence of end capping groups, similar to the conditions normally used to generate fullerenes, thermally stable acetylenic carbon species capped with trifluoromethyl or nitrile groups have been prepared with chain lengths in excess of 300 carbon atoms. Under these conditions, the production of fullerenes is suppressed and only a negligible quantity of fullerenes is produced. Acetylenic carbon compounds are not particularly moisture or oxygen sensitive but are moderately light sensitive. Carbon (13C) nuclear magnetic resonance (NMR) , infrared (IR) spectroscopy, and laser desorption mass spectroscopy are used to characterize these carbon chain species and confirm that capped acetylenic chain polymers, \((-\text{C}≡\text{C})_n\), join graphite, diamond and fullerenes-nanotubes as the fourth allotrope of the element carbon.

The known allotropes of carbon are based either on sp³ hybridization of carbon (diamond) or sp² hybridization (graphite, fullerenes, and nanotubes) .

Although Roald Hoffmann¹) had predicted in the 60s 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 which 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 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 either totally eliminated or substantially suppressed.

The synthesis of mixture of long-chain acetylenic carbon species [\(\eta\)-bis (triethylsilyl) polynyes up to 32 carbon atoms] with alternating single and triple bonds was reported by David Walton and co-workers in 1972⁹) . They had prepared, using copper chloride (Hay coupling) mixtures of acetylenic carbon compounds that contained 2-16 acetylene units:

\[(\text{Et})_3\text{Si}-(\text{C}≡\text{C})_n-\text{Si}(\text{Et})_3\], \(n=2-16\)

Walton proposed that the bulky triethylsilyl groups were useful end groups for stabilizing 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 phase all molecules would have to be oriented in a one-dimensional (linear) manner.]

While our studies have led to the conclusion that acetylenic carbon chains terminated with delocalized electrons (rather than end groups) are extremely unstable⁸ and that hydrogen capped polynyes are normally stable only below room temperature, we have found (see below) that groups bulkier than hydrogen stabilize acetylenic carbon compounds mechanismically. 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 which they believed correlated with increasing alkyne conjugation. For C₃₂, they reported that significantly less than 0.5% of the mixture of compounds produced was of that composition. They also reported that beyond \(\sim C_4\) 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. Francois Diederich and co-workers have also reported the synthesis of mass spectrometric quantities of a C₃₄ alkyne-containing carbon ring ⁰⁰)
by flash heating [18] annulene precursors.

We have prepared a number of model compounds with various end cap group and have studied these with a number of techniques, including NMR (especially $^{13}$C NMR), X-ray diffraction (XRD), IR spectroscopy, high-pressure liquid chromatography (HPLC), and 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) 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°C and 140°C, polynuclear hydrocarbons and graphitic materials begin to form through polymerization.

The crystal structure of this compound reveals the presence of alternating long and short bonds (Table 1 and Fig. 1). The C-7-C-7 distance is 3.502 (±0.0002) 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 brick-like structure. Such a crystal structure was observed and reported recently for a C$_{10}$ acetylenic model compound prepared by Diederich and co-workers.[11]

Table 1 Bond Distances (Å) in (t-butyl) –C$_8$– (t-butyl).

<table>
<thead>
<tr>
<th>Bond Distance</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(13)-C(1)</td>
<td>1.453(9)</td>
</tr>
<tr>
<td>C(22)-C(2)</td>
<td>1.277(9)</td>
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<tr>
<td>C(33)-C(3)</td>
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<tr>
<td>C(44)-C(4)</td>
<td>1.172(8)</td>
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<td>C(55)-C(5)</td>
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</tr>
<tr>
<td>C(66)-C(6)</td>
<td>1.218(9)</td>
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<tr>
<td>C(77)-C(7)</td>
<td>1.363(10)</td>
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<td>C(88)-C(8)</td>
<td>1.202(8)</td>
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<tr>
<td>C(99)-C(9)</td>
<td>1.466(9)</td>
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<tr>
<td>C(101)-C(9)</td>
<td>1.517(8)</td>
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<td>C(111)-C(9)</td>
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<td>C(122)-C(9)</td>
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<td>C(144)-C(13)</td>
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<tr>
<td>C(155)-C(13)</td>
<td>1.525(8)</td>
</tr>
<tr>
<td>C(166)-C(13)</td>
<td>1.536(7)</td>
</tr>
</tbody>
</table>

Scheme 1 The synthesis of (CH$_3$)$_3$C–C≡C–C≡C–C≡C–C≡C–C≡C–C(CH$_3$)$_3$. 

Fig. 1 The unit cell packing diagram of (t-butyl) C$_8$ (t-butyl). 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.
The $^{13}$C NMR spectrum of the (t-Bu) $-C_8$ (t-Bu) acetylenic model compound in solution is shown in Fig. 2 and the resonances from all of the carbon are identified; 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 a room temperature for 1 hour showed no changes in its IR spectra, the XRD pattern, or physical properties. At 60 kbar, a very small amount of graphitization (~2%) was observed. We are optimistic that linear carbons with chain lengths much longer than 300 carbon atoms may be synthesized at such high pressures in future work.

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≡C-Br, begins to form carbon chains at $-56^\circ$C in liquid NH$_3$. We obtained 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 carbon (Fig. 3). This mixture of compounds does not separate on the types of columns used to separate fullerenes (Al$_2$O$_3$) but rather reacts with such columns. The use of HPLC to separate such species is in progress. Mass spectra of mixtures indicates that phenyl capped parent ions for $C_{16}$, $C_{24}$, and $C_{28}$ peaks are produced. A $C_{34}$, cyclic species may also be present in the mixture. Thermal stability studies on the mixtures show

![Fig. 2](image1.png)

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

![Fig. 3](image2.png)

**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. Phenyl peaks occur at 125 ppm.

![Fig. 4](image3.png)

**Fig. 4** (A) The mass spectra of supersonic carbon cluster beams by Kaldor and coworkers (lower molecular weight region)$^{(13)}$. (B) The mass spectra of supersonic carbon cluster beams by Kaldor and coworkers (higher molecular weight region)$^{(13)}$. Note that the average carbon cluster size is $\approx 116$ carbon atoms. [Reprinted from$^{(13)}$ with permission from the American Institute of Physics.]
that the compounds in this mixture are also stable to at least 130°C.

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 Kolder (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. 4 (B) 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" which 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.

It has been known for some time that lower molecular weight carbon clusters may be capped in the gas phase with end groups such as C≡N, hydrogen, and CH₃, beginning with Kaldor et al. who observed K - (C≡C)ₙ-K, 3 ≤ n ≤ 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 Kratschmer-Huffman dimensions, similar mean free paths, and partial gas pressures. Our goal was to cap and thus stabilize these high temperature linear carbon species with trifluoromethyl radicals and nitriles radicals. Helium was used as a third body gas.

Graphite was vaporized using a Spectra-Physics 820 1.5 Kilowatt, C.W., CO₂ Laser into an apparatus shown in Fig. 5 containing a 90% helium: 10% C₂N₂ mixture at 0.2 atm of pressure. Multi gram 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 the walls of the glass reactor, with nitrile groups generated by the plasma sheath associated with the laser use 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 gram quantities were obtained in a 1-hour run. The toluene was then analyzed for fullerenes and other species by ¹³C 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 which may also be produced. The THF was then evaporated under vacuum, and the extracted linear carbon capped species were redissolved in CDCl₃ for ¹³C NMR analysis. A typical ¹³C NMR spectra clearly 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 C₆₀ and C₇₀ was observed. A mass spectral 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 using a Fourier Transform Ion Cyclotron Resonance Mass Spectrometer with a dual cell ion trapping assembly controlled by a Nicolet 1280 Data Station including 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

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**Fig. 5** Apparatus used for syntheses of high molecular weight capped acetylenic carbon chains. The CO₂ laser power in this experiment was 1.3 to 1.5 KW. The dimensions of the apparatus were 19 cm (diameter) × 35 cm (height).

1. Pyrex reactor
2. To vacuum pump
3. Graphite rod
4. Graphite block
5. 1.5 KW laser
6. ZnSe window
7. O-ring
8. Cooling coil
9. Argon (or Helium)
10. C₂F₆ (or Cyanogen, the dash line only for cyanogen reaction)
11. Electrode (only for C₂F₆ reaction)
12. Radio-frequency generator

**Fig. 6** The ¹³C NMR spectra in deuteroacetone of C≡N capped acetylenic carbon chains.
the nitrile 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 trifluoromethyl radicals are used as capping agents, the carbon isotope pattern is still complicated but each carbon cluster becomes more distinct (see Fig.8).

Although it is apparent from the complexity of the mass spectrum that nitrile capping groups may be in place, even the high-resolution spectra at C₈₀ to C₁₀₀ are not definitive. In both the C≡N experiments and the CF₃ 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 CDCl₃ of the capped acetylenic carbon chains, however, show definitive evidence for nitrile end groups that appear as a multiplet between 2337 and 2362 cm⁻¹.

In 1988, Kaldor, Cox and Reichmann again vaporized carbon to produce carbon clusters but used argon, a heavier third body gas (Fig.9). 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 current. The "composite mass spectra" of this type show more accurately the relative intensities in the spectrum. The fullerenes, C₆₀ and C₇₀, are dwarfed in the spectrum by a plethora of peaks with a mean carbon cluster size of 300 carbon atoms. Kaldor's central conclusion from this spectrum was that C₆₀ constituted less than 0.001 of the ion current.

We believed that these clusters in the 1988 Kaldor work were long acetylenic chain compounds with delocalized electrons on either end. We therefore did a capping experiment with both trifluoromethyl radicals and later with cyanogen designed to produce capped 300 carbon atom chains. To generate trifluoromethyl radicals, hexafluoroethane was passed through a 10MHz radiofrequency discharge with about 20 watts of power applied. This produces a very clean mixture of 99% trifluoromethyl radicals and 1% pentafluoroethyl radicals. The experiment was conducted in a slightly different manner than the cyanogen preparation previously discussed. With the trifluoromethyl radicals, we know such 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 -96°C and first condensed a considerable amount of trifluoromethyl radicals on the walls. We then vaporized the carbon and periodically would turn off the vaporization source to condense more trifluoromethyl radicals on the walls, thus sandwiching the trifluoromethyl radicals.

![Fig.7](image1)

**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.

![Fig.8](image2)

**Fig.8** The Fourier transform mass spectrum of CF₃ end capped acetylenic chains produced with He as a third body gas.

![Fig.9](image3)

**Fig.9** The 1988 mass spectrum of carbon clusters produced by Kaldor and coworkers using argon as the third body gas. Note that the average carbon cluster size is ~325 carbon clusters. [Reprinted from with permission from the American Institute of Physics.]
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 trifluoromethyl radicals and carbon chain ends as the mixture is warmed in addition to the capping reactions which occur in the gas phase. Again in this experiment we work at ~0.2 atm of argon so that we could expect to be in concert with the results of Kaldor et al.\textsuperscript{(18)} which produced a mean carbon cluster size of 325 carbon atoms.

Initially the reaction products after warming were dissolved in toluene then subsequently in THF to purify the acetylenic carbon species. The products obtained are amber to dark brown in color. On many runs with the trifluoromethyl capping procedure, there was no detectable fullerene production, whereas on other runs we see small amounts in the toluene fraction. The THF extracted sample was then redissolved in deuteroacetone and the $^{13}$C NMR spectrum (Fig.10) 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 Fourier transform IR spectrum was run on the sample in deuteroacetone and the deuteroacetone was then subtracted from the spectrum. A very strong band at 1200 cm$^{-1}$ obscuring some of the C≡C bending modes of the linear carbon chain provided definitive evidence of trifluoromethyl substitution. A $^{19}$F NMR spectrum in CDC\textsubscript{13} showed a strong sharp signal for trifluoromethyl groups at ~54.7 ppm from CFCl\textsubscript{3}.

Next the THF extract was coated onto a solid probe and the solvent vaporized from the probe. The Fourier transform mass spectrometer with the Nd : YAG 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.11) with carbon isotope patterns 24 mass numbers apart.

We ran a number of experiments with the same synthetic apparatus and procedures but omitting trifluoromethyl or nitrile capping groups. Fullerenes including C\textsubscript{60} and C\textsubscript{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 Kratschmer-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\textsubscript{60} and C\textsubscript{70}. If one looks in Table 1 it is apparent that there is chain curvature in the crystal structures of model compounds. We view the diradical linear carbon chains to frequently exist in spiral-like chain structures as shown in Fig.12.

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

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Fig.10 The $^{13}$C NMR spectra in deuteroacetone of CF\textsubscript{3} end capped acetylenic carbon chains.

Fig.11 The Fourier transform mass spectrum of CF\textsubscript{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.

Fig.12 The Spiral Zipper Hypothesis.
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a series of zipper-like reactions. Some become fullerenes and other 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 mass spectrometry experiments\(^{99}\). Subsequently there has been work by Jarrold and co-workers in which the same species were labeled "polycyclic polyyne ring isomers"\(^{200}\). They have studied carbon clusters ranging from 50 to 70 carbon atoms in size "annealing" 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 and groups. They are molecular allotropes. Both diamond and graphite surfaces are terminated with hydrogen, hydroxyl, or oxide end groups\(^{11}\).

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 length of about 300. Another very interesting observation is the fact that 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 easily collected off the walls even without the use of solvents while 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. 9) in which Kaldor et al.\(^{19}\) 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 completely novel feature for any form of carbon and should lead to many technological applications, including carbon coatings, possibly activated by UV light. Further, since 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. This new form of carbon will be proven to be the most reactive room temperature stable form of elemental carbon and as such will have an extensive reaction chemistry. Linear carbon could also be used as a zero hydrogen fuel in fuel cells based on oxygen combustion. There is no doubt also that many more end groups will be found to stabilize acetylenic carbon. In fact, at this writing, we feel that most organic end groups and perhaps many inorganic end groups will stabilize linear carbon.

Reference

2) A form of carbon called "carbyne" has been reported\(^{3}\), but other workers have extensively studied their evidence (4-7) and this contention is generally held to be incorrect.
3) V. M. Mel'nichenko, B. N. Smirnov, V. P. Varlakov, Y. N. Nikulin, A. M. Sladkov, *Carbon* 21, 131 (1983), and references contained therein.
7) M. F. Hawthorne, Preliminary Reports, Memoranda and Technical Notes of the Materials Research Council Summer Conference, La Jolla, California, July 1973 (NTIS).
9) A more detailed study is planned. It appears that such radical terminated species are unstable above \(-100\)°C.
24) The RJL laboratory is grateful for substantial support from the Air Force Office of Scientific Research grant F49620-92-J-0104, the U. S. Department of Energy Advanced Research Projects Agency grant DE-FG05-91ER12119, the National Science Foundation grant CHE-9106482 and the Robert A. Welch Foundation grant F-0700. Unfortunately this project was too speculative in its early stages to received funds targeted directly toward linear carbon.