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The Formation of Long Carbon Chain Molecules during Laser Vaporization of Graphite

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Abstract: Graphite is laser vaporized into a He carrier gas containing various simple molecules such as H_2, H_2O, NH_3, and CH_3CN, supersonically expanded, and skimmed into a molecular beam, and the beam is interrogated by photoionization time-of-flight mass spectrometry. Without added reactants in the He carrier gas, C_n species up to $n = 130$ are readily observed. Two distributions separated at about $n = 40$ appear to be present with the low n species the focus of this work. In the presence of added reagents, new species appear as a result of reaction. These are satisfactorily explained on the basis that a significant proportion of the C_n species initially formed are reactive radicals with linear carbon chain structures which can readily add H, N, or CN at the ends to form relatively stable polyynes or cyanopolyynes. Some of the cyanopolyynes detected have also been observed in the interstellar medium, and circumstellar carbon condensation processes in the atmospheres of carbon-rich stars similar to those studied here are suggested as possible synthetic sources.

At present the most successful schemes for interstellar molecule formation are those which propose that bimolecular ion–molecule processes occur in the cold gaseous dark clouds where they are detected.[1,2] Although the abundances of many small molecules can be satisfactorily explained by this theory,[3,4] it is far from clear that they offer a plausible route to the long-chain polyynes, HC_nN ($n = 3-11$), that have been observed in significant amounts.[5-9] Even some of the largest and most complete attempts to explain the range of molecules observed are not able to extend much past HC_3N, i.e., species such as HC_5N cannot be included in a totally satisfactory manner without a great increase in the scale of the calculation.[10] Clearly other mechanisms for the formation of these molecules need to be explored. One plausible mechanism might be the formation of these species by bombardment of carbonaceous grains by energetic neutral atoms. Devienne and Teisseire[11] have carried out an interesting experimental study which produced several of the long carbon chain species of interest here by such bombardment of graphite.

The long-chain molecules are detected not only in cold molecular clouds but also in the atmospheres of certain stars such as the cool carbon rich red giant IRC+10216.[9,12] In addition to ejecting the polyynes (and many other molecules) into the general interstellar medium, such stars also appear to eject carbon particles.[12,13] It thus seems appropriate to consider an alternative scenario for the formation of carbon chain molecules which involves conditions that relate more closely to those that occur in stellar atmospheres in which carbon is condensing.[12]

The present study was initiated primarily to explore the particular possibility that long carbon chain molecules, such as the cyanopolyynes that have actually been detected in the interstellar medium (ISM), can form under conditions in which carbon vapor nucleates in the presence of hydrogen and nitrogen, conditions similar to those which are expected to occur in the atmosphere of a carbon star. With this objective a series of experiments was undertaken in which carbon was laser vaporized into a helium stream containing various added gases, allowed to cluster and react, and studied by photoionization mass spectrometry. The astrophysical implications of the present experiments will be considered in more detail elsewhere[14] and will be described here only briefly.

There have been a number of important previous studies of carbon clustering. Some early mass spectrometric measurements[15,16] detected carbon clusters with up to 33 atoms in carbon vapor. More recent experiments have shown that much larger clusters with more than 100 atoms can also form,[17-19] and convincing evidence for linearity of the even clusters, C_n, in the size range $1 < n < 24$ has been obtained.[17] Study of the larger clusters has shown that some of the larger clusters, particularly C_{60}, have some unique properties[19-22] which are most readily explained if they are inert hollow spheroidal shell molecules. Moreover, a laser vaporization cluster beam[23] study indicates that macroscopic particles also form, in addition to the long-chain molecules and large spheroidal clusters. These discoveries also give insight into the homogeneous nucleation mechanism governing the formation of carbonaceous particles such as soot and carbon black and the explanation which they provide for the resultant morphology of these particles.[21]

The work presently described concentrates on the smaller carbon clusters with from 6 to 30 atoms and some reactions which they undergo. There has been much conjecture about the structures of these clusters: whether or not, for instance, they are linear carbon chains or monocyclic rings.[16] Odd/even variations of intensity in mass spectrometric data have been interpreted in terms of linearity.[16,24] However, some of the mass spectrometric data

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indicated that clusters which had $4n + 7$ (n = 1–4) atoms might have special stability. This so-called "Δn = 4 effect" has been considered as possible evidence for ring structures.[16,25] However, there is convincing evidence that the even clusters with $n < 24$ are linear[17] and our results strongly support this conclusion for at least a significant fraction of the species in this range detected.

Experimental Section

A detailed description of the apparatus used in this study has been given previously.[23,26-29] A 2.5 cm diameter disk, cut from 0.3 mm sheet of high-density graphite, was mounted so that the vaporized products formed at its surface by a focused pulsed laser can be entrained in a pulse of He carrier gas just before it expands through the throat of a supersonic nozzle. The disk was rotated and translated during the experiments so that fresh surface was continuously exposed to the laser (30–40 mJ of 2nd harmonic Nd:YAG laser radiation focused to a 0.1-mm spot) which was fired to coincide with the peak in the He gas density over the target area. The gaseous products flowed via a channel (2 mm wide expanding after 13 mm to 4 mm for a further 10 mm) into a large vacuum chamber. The supersonic jet of He entrained clusters so produced was skimmed 30 cm downstream to form a beam which passed through two further stages of differential pumping into the ionization chamber of a time-of-flight (TOF) mass spectrometer. At this point the cluster population was interrogated by a second pulse of ionizing ArF excimer laser radiation (10 mJ at 6.4 eV), which could be fired to synchronize with the characteristic arrival times of the clusters, producing ions whose masses were determined by TOF mass spectrometry. The main timing sequence is controlled by an IBM-AT microcomputer interfaced to a microsecond delay generator via a CAMAC crate. In general an individual experiment yielded a mass spectrum averaged over a sequence of ca. 1000 cycles repeated at 0.11-s intervals.

In the initial experiments pure He entraining gas was used, producing the basic carbon cluster distribution. To carry out the reaction studies, carefully controlled amounts of reactants were introduced into the He. In order to do this, the various gas flow rates were monitored by separate floating ball flowmeters and, in especially critical cases, a Hastings Teledyne digital flowmeter was also used to monitor the reactant. The H_2 and N_2 reactants as well as the He were filtered whereas the O_2/He mixture was used directly. Experiments with water were carried out by passing the He through a steel capsule containing cotton wool soaked in either H_2O or D_2O. The He backing pressure and capsule temperature were adjusted to achieve estimated water/He mixtures of ca. 1/1000.

Results

A typical cluster mass distribution without added reactants (obtained using ArF laser photoionization) is depicted in Figure 1a. It should be noted that, as discussed above, clusters with more than 30 atoms are also observed, which behave in a different way[19-22] from the smaller ones which are considered in this study. The curious prominence of C_{11}, C_{15}, C_{19}, and, to some extent, C_{23} (the Δn = 4 effect) is clearly evident. The ring hypothesis is considered further in the Discussion section.

In the following sections we describe the results obtained when various reagent gases are added to the gas stream. These gases are exposed to the very high plasma temperatures and are presumably partially decomposed into very reactive atomic and free radical species which are in turn the major reactants with the carbon clusters.

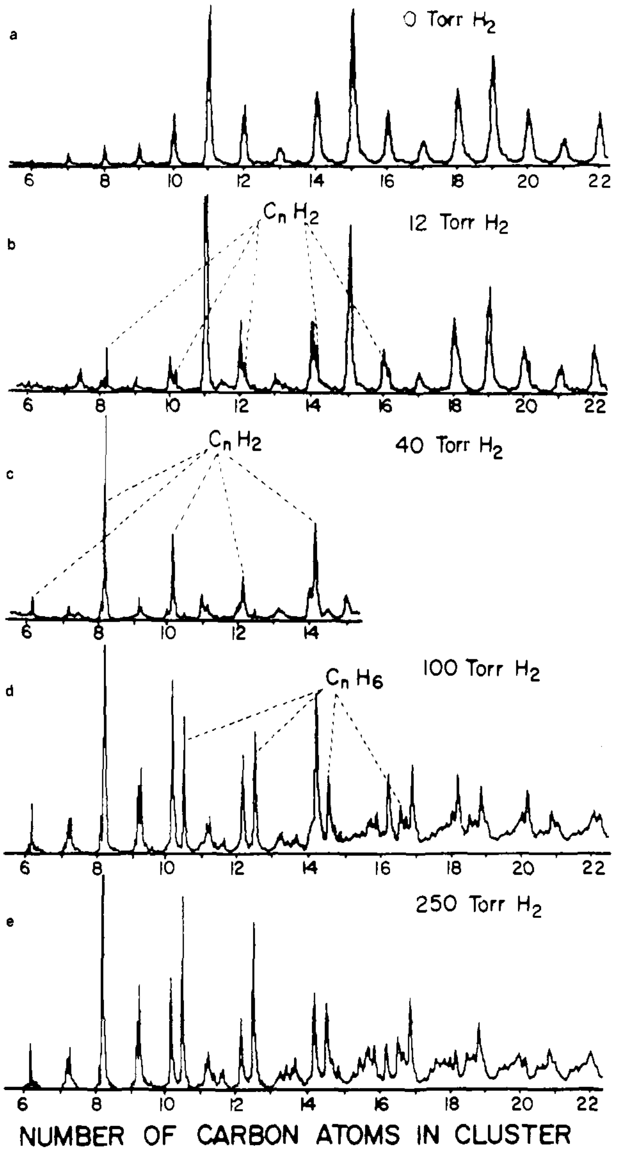

Figure 1. (a) Mass spectrum of bare carbon clusters, from C_5 to C_{22}, produced in the presence of a pure He pulse. (b) Result obtained when ca. 12 Torr of H_2 is entrained in the He (ca. atmospheric pressure in general) pulse. The even n peaks grow +2 mass unit satellites producing peaks corresponding to C_8H_2, $C_{10}H_2$, $C_{12}H_2$, $C_{14}H_2$, $C_{16}H_2$, and $C_{18}H_2$ which can be clearly identified. Note that C_8H_2 is strong almost immediately even though C_8 is very weak in spectrum a. (c) When ca. 40 Torr of H_2 is entrained the mass spectrum contains essentially only hydrogenated products. Note that the odd carbon clusters which are still bare in spectrum b have now reacted, indicating that although they are reactive they are slightly less so than the even ones. The most striking changes are the following: the strength of the C_8H_2 peak in view of the insignificance of the bare C_8 cluster in spectrum a, the appearance of extra peaks for other even clusters, and the dramatic collapse of the C_{11} and C_{15} peaks. (d) In this scan 100 Torr of H_2 were entrained in the He. We note that for the even clusters the C_nH_2 peak for a given even n value gradually loses its dominance as n increases though the peak for $C_{18}H_2$ is clearly identifiable. For n = 10 and 12, C_nH_6 are becoming the dominant peaks and for n = 16, 18, and 20 the C_nH_{10} peaks are becoming dominant. The odd n cluster peaks have been replaced by groups of weak peaks corresponding to a varied range of hydrogenated products. The range is narrow for low n where only a few sharp peaks are observed and wide at high n where unresolved broad signals are detected. (e) When 250 Torr of H_2 are entrained, the dominant peaks (for even n species) are the following: C_6H_2, C_8H_2, $C_{10}H_6$, and $C_{14}H_2$ and $C_{14}H_6$, $C_{16}H_{10}$, $C_{18}H_{10}$, and $C_{20}H_{10}$. In general no single species is dominant for the odd n set though C_7H_2, C_9H_2, and C_9H_3 do stand out.

Reactions with H_2. The results of the reactions which occur when various amounts of H_2 are entrained in the He pulse are presented in Figure 1, spectra b–e, in which the ratio of H_2:He is varied. When a small amount (12 Torr) of H_2 is entrained (Figure 1b), relatively marked changes are detected immediately. The first noticeable result is that peaks appear at C_nH_2 with n = 8, 10, 12, and 14, and by the time 40 Torr have been introduced (Figure 1c), the dominance of C_{11} and C_{15} has been wiped out and replaced by the dominance of the C_nH_2 species (n even). In fact clear evidence for C_6H_2 and C_8H_2 is obtained whereas the bare C_6 cluster is barely detectable and C_8 is very weak indeed

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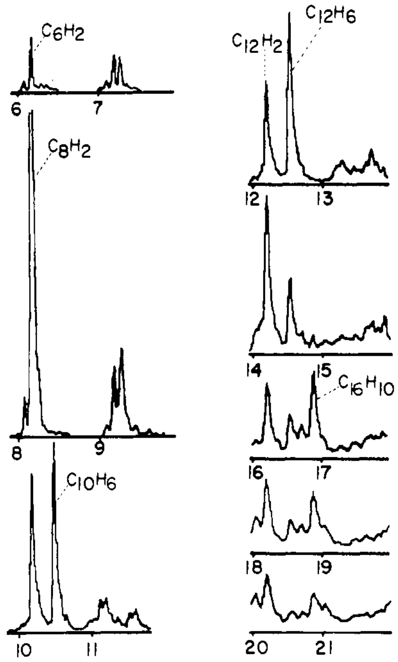


Figure 2. In this detailed re-presentation of Figure 1, spectrum d, the products of hydrogenation can be compared as a function of increasing mass number. It is particularly striking that the first mass peak to be observed, C_nH_2, remains strong for all even n values. C_nH_6 peaks are not observed for $n < 10$, and as n increases, this peak becomes weaker. Peaks at C_nH_8 and C_nH_{10} appear at $n = 14$ and 20, the latter tending to share dominance with the C_nH_2 features. The odd clusters behave in a much more irregular manner forming a range of hydrogenated products showing no particularly striking specificity.

in Figure 1a. In the 100-Torr H_2 experiment, Figure 1d, strong peaks are also observed for $C_{10}H_6$, $C_{12}H_6$, and $C_{14}H_6$ (weaker features are also detected as discussed below). Even more striking changes take place in the case of the odd n clusters. In Figure 1c we see that the bare cluster peaks (including those for the dominant C_{11} and C_{15} species) have disappeared completely to be replaced by groups of relatively weak features due to sets of hydrogenated products.

As the H_2 concentration is increased (Figure 1, d and e), C_nH_6 products begin to become prominent for n even and >8. The essentially complete inertness of the C_8H_2 species to further addition of hydrogen under these conditions is very noticeable. Some detailed aspects of the reaction are effectively highlighted in Figure 2 where the results of Figure 1d are displayed so that the products for successive odd and even n species can be compared in a vertical scheme. In this diagram, we find that, for even n, the C_nH_2 signal is in general always relatively strong and that the C_nH_6 signal, which only appears when $n = 10$ (for which it is strong) or more, gradually diminishes as peaks at C_nH_8 and particularly at C_nH_{10} appear as n increases from 14 to 20. The strength of the C_nH_2 peak diminishes much more rapidly with increasing n at high H_2 concentrations as can be seen from Figure 1, d and e. The dominant peaks for a given even n value are, in addition to C_nH_2, the following: $C_{10}H_6$, $C_{12}H_6$, $C_{14}H_6$, $C_{16}H_{10}$, $C_{18}H_{10}$ and $C_{20}H_{10}$.

The behavior of the odd n species can also be followed as a function of increasing n in Figure 2 where it is seen to be rather more complicated. The general result is that these species react rapidly (though not quite as rapidly as the even clusters) to form a whole range of feasible hydrogenated hydrocarbons, including ones with odd numbers of hydrogen atoms.

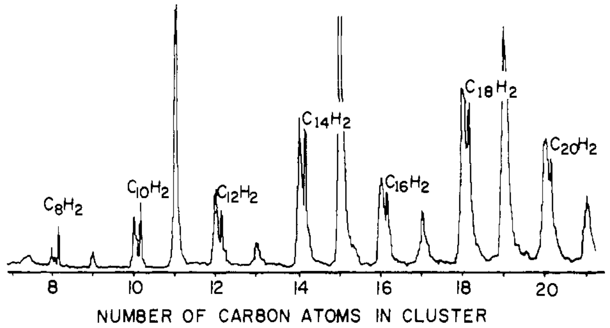


Figure 3. When water vapor is entrained in the He, very clear +2 mass unit satellites are observed on the even n peaks. These peaks are sharp relative to the bare cluster signals which may signify stability to ion fragmentation. In this experiment there is no obvious loss of the general underlying pattern of intensities which characterizes the bare cluster scan, Figure 1a. In this respect the water reaction appears to be very similar to the H_2 experiment whose results are shown in Figure 1b. In particular we note that C_{11}, C_{15}, and C_{19} remain dominant and apparently are fairly unreactive. In addition it appears that under these conditions the reaction has not proceeded further than the formation of C_nH_2 species.

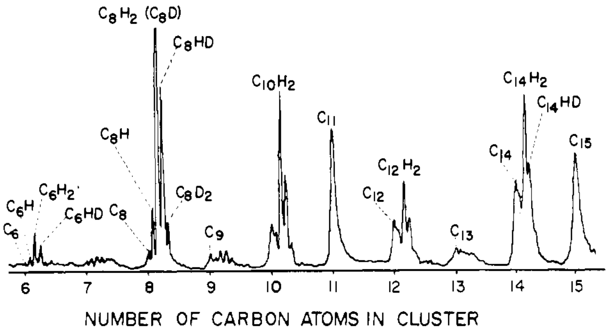


Figure 4. In this detailed scan the results obtained by using a D_2O/H_2O mixture entrained in the He pulse are presented. The degree of reaction is somewhat greater in this scan than in Figure 3. The even n peaks form the predicted species: C_n, C_nH, C_nD, C_nH_2, C_nHD, and C_nD_2. Although C_7 and C_9 have reacted and show satellites, C_{11} and C_{13} have not and C_{13} is, as usual, a weak broad feature.

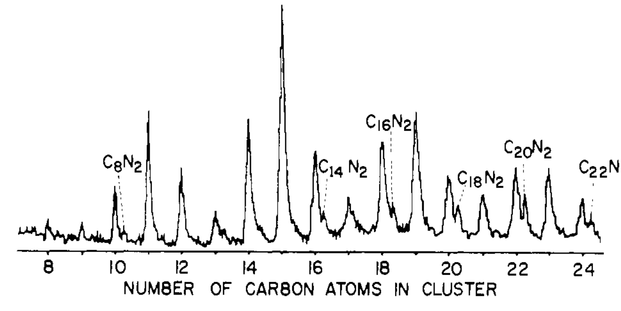


Figure 5. In this scan the results of introducing N_2 into the He pulse are shown. Although the general pattern characteristic of the bare carbon cluster distribution is detected, one observes that the even species peaks are accompanied by satellites at +4 mass units. These correspond to the formation of the symmetric dicyanopolyynes, $N{\equiv}C{-}(C{\equiv}C)_n{-}C{\equiv}N$.

Reactions with H_2O. The results of the reactions that take place with trace quantities of water are nicely displayed in Figure 3 where unequivocal evidence for the formation of species with the formula C_nH_2 for $n = 10, 12, 14, 16, 18, 20$ is presented. The mass spectrum is very similar to that obtained with small amounts of H_2 as depicted in Figure 1b. These two sets of data are clear evidence that the even n clusters are linear as the most obvious interpretation is that the products are polyynes of structure $H(C{\equiv}C)_mH$. Further confirmation of this interpretation is furnished by the results of the mixed D_2O/H_2O experiment shown in Figure 4. Here the peaks are readily assigned as corresponding to C_n, C_nH, C_nH_2 + C_nD, C_nHD, and C_nD_2 as expected.

Reactions with N_2. The results of the reaction with N_2 are shown in Figure 5 where each even n carbon peak is seen to develop a +4 mass unit satellite. This observation is readily interpreted as due to the formation of the *di*cyanopolyynes, presumably produced by N atom addition to the two ends of the even carbon atom chains. The data are thus convincing evidence for the production of $N{\equiv}C{-}(C{\equiv}C)_m{-}C{\equiv}N$ molecules, with m = 7–10, and also a further excellent indication that linear carbon chains are present.

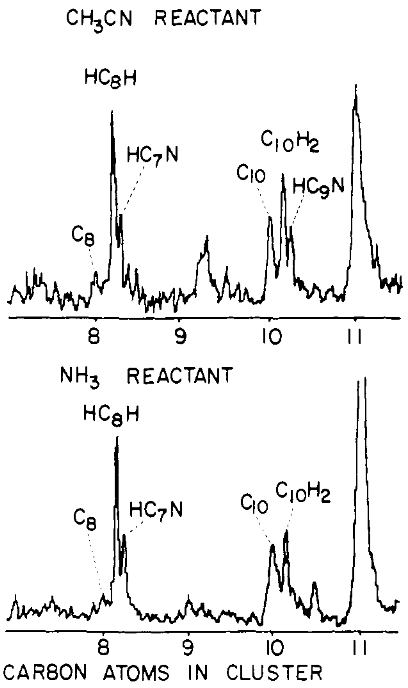


Figure 6. In the upper scan is depicted the result of introducing CH_3CN into the He pulse. This molecule is expected to provide both H atoms and CN radicals which are expected to react with the even carbon chains to produce the polar cyanopolyynes. In this scan the C_8 and C_{10} peaks are accompanied by peaks at +2 and +3 mass units consistent with polyyne formation and also +3 mass units consistent with cyanopolyyne formation. The latter peaks belong to HC_7N and HC_9N, both of which have been detected in the interstellar medium. In the lower trace the results of introducing NH_3 into the He are depicted. In this case H and N atoms are expected to react with the odd carbon cluster population to produce the cyanopolyynes. Clear evidence for HC_7N is observed as well as for HC_8H and $HC_{10}H$ although the HC_9N signal is very weak.

Reactions with CH_3CN and NH_3. The reactions between the carbon clusters and reactants that can introduce hydrogen and nitrogen into the system at the same time offer the possibility of producing the polar cyanopolyynes such as HC_7N and HC_9N that actually have been detected in the ISM. In addition the interesting possibility of producing them from either the odd *or* the even *n* bare carbon cluster populations presents itself. In the upper trace in Figure 6 the result of introducing CH_3CN into the He is depicted which shows clear evidence for the production of HC_8H, HC_7N, $HC_{10}H$, and HC_9N. In the plasma it is likely that CN radicals will be formed in significant quantities as well as H atoms. Thus it is likely that a significant fraction of polar cyanopolyynes is produced by addition of H and CN to opposite ends of an *even* linear cluster population. In the lower trace of Figure 6 is depicted the result of adding NH_3 which shows similar products, though the HC_9N peak is rather weak. In this case it is possible that the cyanopolyynes are produced by addition of H and N atoms to opposite ends of *odd* numbered carbon chain species (if such exist).

Discussion

In this study, there are two major sources of concern in interpreting the observations. First, we are assuming that the dominant reactions involving entrained reagents take place after carbon has clustered so that the detected products are reliable probes of the properties of the pure carbon clusters. However, the possibility exists that H atom reactions take place at an early stage in the clustering process and produce intermediates which guide the clustering process toward the formation of linear polyynes. This seems unlikely because the carbon plasma at the point of ejection is constricted at the high He pressure (ca. 1 atm), diffusion is slow, and the carbon clustering reactions are very rapid in the resulting plume of concentrated carbon vapor.

Second, in the interpretation of some of the pertinent mass spectrometric observations we have assumed little fragmentation. As is discussed below, our results suggest that fragmentation may be extensive for the bare clusters and thus may be responsible for the $\Delta n = 4$ effect. The mass spectra of the even *n* reaction products, however, seem to consist largely of parent ions, since the major product ion peaks can be accounted for by saturated valence compounds. In summary, we believe that the peaks for the even *n* products are reliable probes of the original neutral bare parent clusters.

The major specific result of this series of experiments is highlighted by the result of the reaction with water depicted in Figure 3 where unequivocal evidence that there are only two highly reactive monovalent sites on the even bare clusters from $n = 8$–20 is presented. This result is most readily explained if the initial products formed from the even *n* clusters are the stable polyynes resulting from the addition of a hydrogen atom to each end of a polyyne chain diradical according to the scheme

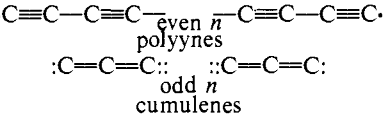
$$(C\equiv C)_m \xrightarrow{H} (C\equiv C)_m{-}H \xrightarrow{H} H{-}(C\equiv C)_m{-}H$$

The results of the reactions with small amounts of hydrogen, Figure 1b, are much the same, suggesting further confirmation of this proposed explanation. It is interesting to note that the C_nH_2 peaks are quite sharp relative to the bare clusters in Figure 3. One possible reason for this is that the bare cluster ions are metastable and fragment in the flight tube whereas the polyynes, which are relatively stable gas-phase species, produce parent ions which are not fragmenting.

At higher hydrogen concentrations, additional hydrogen atoms add to the larger even clusters four at a time. This can be rationalized in terms of linear polyyne chains in which triple bonds are being reduced to a single bond. This may be a consequence of a tendency of triple bonds to exhibit somewhat lower reactivity than double bonds under these conditions.

A further interesting observation on the general reactivity behavior of the various clusters is the inertness of C_8H_2 to further reaction. In Figure 1 we see that the bare C_8 signal is weak in Figure 1a and by Figure 1b it is the C_8H_2 peak which is the dominant feature. At the highest hydrogen pressure the whole spectrum is dominated by the C_8H_2 signal as this species does not seem to undergo further reaction. This suggests that under these conditions, conditions under which the longer chains are hydrogenated, C_8H_2 (and to some extent also C_6H_2) is extremely stable. This behavior is intriguing as it is in apparent contrast with the behavior of the higher even *n* C_nH_2 homologues. As indicated in Figures 1 and 2, the clusters C_{12}, C_{14}, and C_{16} clearly give rise to prominent C_nH_6 peaks as well as C_{14}, C_{16}, C_{18}, and C_{20} higher products. This observation indicates that there is a change in behavior after $n = 8$; however, the reason is still not certain. It may be possible that there is more than one isomer of C_n $n > 9$ (as was found[30] recently for C_7^+) with only a portion of the $n = 10$ and higher clusters being linear.

Comparing the odd cluster reactivities with those of the even ones, the mass spectra for the reaction products appear to display an odd/even alternation. Although it is possible that the odd clusters are not linear, the expected chemical differences between even *n* polyynes and odd *n* cumulenes



$$\cdot C\equiv C{-}C\equiv C\underset{\text{even } n}{-\!-}C\equiv C{-}C\equiv C\cdot$$
$$\text{polyynes}$$
$$:C{=}C{=}C::\quad ::C{=}C{=}C:$$
$$\text{odd } n$$
$$\text{cumulenes}$$

can explain the differences between odd and even cluster behavior. Cumulenes would certainly be expected to yield a more complicated range of initial products. Pitzer and Clementi[24] suggest that the even chains also possess cumulene-type bonding in their ground states; however, the present results are consistent with polyyne-like reactivities.

The $\Delta n = 4$ effect is strikingly depicted in Figure 1a where the characteristic pattern for the mass spectrum of the bare clusters is shown. On the basis of the hydrogen reaction results, however,

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we observe that the bare C_9, C_{13}, and C_{17} peaks are replaced by hydrogenated product peaks which are similar both qualitatively and quantitatively to those which result from C_{11}, C_{15}, and C_{19} even though the bare peaks of the former set are at least an order of magnitude weaker than those of the latter. In fact the resulting features vary rather gradually in pattern *and* intensity across the range of odd *n* products. Because we cannot interpret the hydrogenated peaks for odd *n*, it is not clear whether we are observing parent ions. However, the smooth variation of ion intensities with *n* (odd) suggests that the neutral precursors are more closely related in character than the original $\Delta n = 4$ pattern implies. This suggests that the characteristic intensity pattern of the mass spectrum observed for the bare clusters in Figure 1a may be dominated by ion fragmentation and is not a true diagnostic of the neutral cluster relative abundance. The $\Delta n = 4$ effect may be due in some way to ring structures—probably of the *ions* ultimately detected.

After the work detailed here was completed the interesting experiments of Devienne and Teisseire[11] were brought to our attention. Their observations and ours are complementary as they have shown that, given carbonaceous grain (graphitic) particles, a range of interstellar species can be produced by grain bombardment with high-energy neutrals.

In the present experiments we conclude that such species can be formed more or less simultaneously with carbonaceous grains. Although the conditions in our experiments differ from those in stellar atmospheres, it is highly likely that the main features of the carbon nucleation process are similar. Therefore, we feel that these experiments demonstrate a simple way in which the long-chain cyanopolyynes observed by radioastronomy can be formed in regions where carbon is condensing, and in the absence of any alternative similarly convincing interstellar process, the results suggest a different source of these species from those heretofore considered.[12,11]

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Is Delocalization a Driving Force in Chemistry? Benzene, Allyl Radical, Cyclobutadiene, and Their Isoelectronic Species

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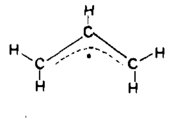
Abstract: The VB correlation diagram model (Figure 1) is used to answer the title question. It is shown that *only atoms that form weak two-electron bonds with low triplet excitation energies may generate delocalized species that are stable toward a localizing distortion.* Electronic delocalization is, then, seldom expected to be a significant driving force in chemistry. By this principle, the π-components of delocalized species, like C_6H_6 and C_3H_5, are predicted to be distortive electronic systems that are trapped, within "rigidly" symmetric σ-frames, and are thereby delocalized despite their opposite inherent tendency. The predictions are examined by means of ab initio investigations at the levels of STO-3G, 6-31G, and 6-311G with extensive correlation (CI) calculations (up to 6×10^6 determinants). σ–π energy partitions show that the π-components of C_6H_6 and C_3H_5 are indeed distortive much like the π-electrons of C_4H_4, and all the π-components resemble, in turn, their isoelectronic H_n ($n = 3, 4, 6$) species in the common reluctance to adopt geometries that lead to electronic delocalization. *Electronic delocalization* in C_3H_5 and C_6H_6 *turns out to be a byproduct of the σ-imposed geometric symmetry and not a driving force by itself.* The π-distortive propensities are shown to coexist harmoniously with the thermochemical stability of benzene and the rotational barrier of allyl radical. Further application of the model shows that π-delocalization, per se, is seldom expected to be a driving force in organic molecules containing C, N, and O. In this manner the delocalization problem is unified and shown *not* to be merely a matter of electron count and mode of delocalization.

In recent communications,[2] ab initio computational evidence has been provided that the π-electrons of allyl radical (**1**) and benzene (**2**) prefer to distort to their localized π-components, much like the π-electrons of singlet cyclobutadiene (**3**). These distortive propensities in **1** and **2** are, however, quenched by the σ-frames that strongly prefer regular geometries with uniform C–C bond lengths. Consequently, π-electronic delocalization in **1** and **2** turns out to be a byproduct of a geometric constraint and occurs despite the opposite inherent tendency of the π-electrons. This result touches a key question of chemical epistemology: is electronic delocalization a driving force of stability and geometric shape? Our preliminary computational data[2] show that, in organic species, π-delocalization is not such a driving force but rather a byproduct phenomenon.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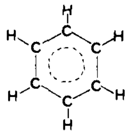
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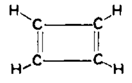
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The credibility of this conclusion must be established now by a two-pronged examination. Firstly, it must be shown that it is not a computational artifact but rather a chemical trend that emerges from the broader context of chemistry. Secondly, the

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