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The chemistry of the interstellar medium

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There has been a dramatic advance in our appreciation of the richness of the molecular component of the interstellar medium, mainly brought about by combining laboratory spectroscopic measurements with radioastronomy search programmes. We now know that vast hordes of molecules lurk deep in the black clouds strewn among the stars of the Galaxy. They range from commonplace small species such as water and carbon monoxide through organic ones such as alcohol and formaldehyde to highly reactive ions and free radicals which are intermediates in the production of more complex molecules. The study of the microwave and infrared signals from these molecules has revealed, for the first time, the intimate details that surround the birth of a star.

Some intriguing and rather exotic molecules, consisting primarily of carbon atoms connected in long chains, have also been identified. Not only are these curious molecules to be found in the cold tenuous dark clouds but they are also to be found streaming out of carbon-rich stars into the surrounding interstellar medium. Such stars also appear to be emitting copious quantities of dust. Laboratory experiments, stimulated by these observations, have led to the discovery of the hollow spheroidal carbon molecule, C_{60} buckminsterfullerene. This discovery has not only provided the key to the mechanism of formation of small carbon particles (such as soot) but also the first detailed understanding of their structure. These processes and the species that result may be directly related to those involved in the formation of the primordial macroscopic particle.

Introduction

One of the most exciting advances in astrophysics in recent years has been provided by the breakthrough in our ability to detect molecules in space by radio and infrared techniques. Although the first interstellar molecules were identified more than fifty years ago it was not until the radio detections of ammonia and water by Cheung *et al.* (1968, 1969) that the possibility of detecting commonplace molecules became feasible. The molecules detected earlier were free radicals found in regions of space which were essentially transparent to visible starlight. Their detection was somewhat misleading in that it suggested that more commonplace molecules might not be able to survive destruction by the ambient radiation which pervades the space between the stars. What had been overlooked, however, was the fact that in the regions that are opaque, such as the interiors of the cold dark clouds, which Barnard (1927) had photographed so beautifully, there was essentially no radiation. It must be pitch black inside these clouds and as a consequence any molecules formed would be protected from photodissociation. The stumbling block towards early progress seems to have been a lack of awareness that molecules might have been formed at all in these regions.

The discovery of many different molecules in a wide range of astronomical objects has had a significant impact on a diversity of astrophysical problems. Molecules are now used as the most effective probes of the spiral structure of our own Galaxy. As the Solar System lies some 30000 light years from the centre of the Galaxy and more or less in the plane, one can only see the stars that lie within a radius of about 6000 light years because visible light from further away has been diminished because of scattering by the interstellar dust that also accumulates in the plane. Radio waves are, however, hardly affected and so such signals can be detected from all parts of the Galaxy and particularly from the centre. Radio studies of the demographic disposition and physical condition of galactic CO are now some of the most important indicators of the structure and dynamics of the matter in our own Galaxy. Molecular measurements often provide some of the most accurate gauges of low temperatures and thus such measurements, as for the 3 K background (Thaddeus 1972), impact directly on cosmological questions. Indeed the first measurement of the background radiation temperature, historically, was a measurement on the molecule CN nearly 50 years ago, long before its significance was recognized (McKellar 1941; Herzberg 1950). Studies of the molecular composition of various interstellar clouds have given rise to a new view of the types of chemical reactions that occur in the interstellar medium in general and have initiated some major new experimental methods to understand them (Smith & Adams 1981). These experiments have also had application to upper atmosphere processes. Probably as exciting and important as any other advance has been the new insight that molecular measurements have given on the gaseous dynamics involved in the birth of a star. Such events occur deep in the black clouds and are thus hidden from view optically. During the initial condensation phase, gravitational energy is converted via kinetic energy into internal energy of the molecules which in turn can be dissipated by the emission of microwave and infrared photons. These photons are of sufficiently low frequency that they can readily escape the cloud, cool the embryonic stars, and thus enable further collapse to occur. Of course it is the eventual detection of these photons that allows us to intrude on the earliest phases of stellar birth.

Here after a brief introduction to some of the technical details involved in radio detection the main focus will be a detailed discussion of some very new experimental results, both astrophysical and chemical, involving molecules with high carbon content. These have recently led to a clearer and more detailed understanding of the relation between interstellar grains and the molecules which inevitably accompany them. The experiments have also revealed a major new view of the mechanism of combustion.

ASTROPHYSICAL DETECTION OF INTERSTELLAR MOLECULES

The main technical advance that provided the key to Pandora's Box was the development of sensitive radio telescopes capable of operating at microwave and millimetrewave frequencies, *ca.* 1–200 GHz. As a result, a complicated interstellar chemical scenario has been discovered which appears to be responsible for the production of a range of complicated molecules. As mentioned earlier, the molecules once formed in the black clouds are protected from the dissociating effects of starlight by scattering by the particles responsible for the opacity. The molecules were originally also protected from detection because visible light from background stars could not shine through the clouds to enable their spectroscopic fingerprints to be observed. The molecules are in general so cold (less than 50 K) that emission is very weak and in the radio and infrared ranges which up till recently were inaccessible regions of the spectrum. In these clouds there are also the regions that are so hot that optical and ultraviolet light are

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produced. These are very exciting regions where new stars are forming. However, such objects are so deeply embedded in the black regions that the radiation is trapped and cannot readily escape. Instead it destroys the surrounding cloud gradually dissociating the surrounding cloud of dust and molecular gas into atoms and ions. When such an object has finally eaten its way out of the molecular cloud in which it was born it becomes visible optically as an emission nebulae. Before this stage, however, radio and infrared radiation can reveal the most intimate moments that surround the birth of a star.

The molecular properties that are the medium for the transfer of information are transitions between the molecular quantum states. In fact, molecular energy levels can be divided into three ranges of energy and associated frequency: rotational, vibrational and electronic (in increasing order). We are most concerned with rotational energies (Kroto 1975) that lie between 1 and 200 GHz, populated at temperatures between 5 and 200 K. Light scattering is very sensitive to frequency, in fact it is proportional to the frequency to various powers depending on the size (relative to the radiation wavelength), shape and polarizability of the scattering species. Thus as excited rotational levels are populated even at low temperatures, transitions can occur and the emitted photons, with frequency patterns characteristic of the particular molecules, can pass effectively unhindered out from such clouds. Indeed it is now recognized that, at such low temperatures, rotational transitions are the most important medium whereby the kinetic energy generated by gravitationally induced cloud collapse can escape. It is this energy-dissipation process that allows the gas to cool during the initial stages and enables further collapse and ultimately star-formation to take place.

Laboratory microwave spectroscopy is a very powerful technique capable of detecting small- to medium-size molecules with a certainty that few other techniques can approach. The radio lines are very narrow and occur in characteristic patterns that are so specific to a given molecule that such molecules can be unequivocally identified. Even isotopically substituted speicies or different conformers of the same molecule can be easily differentiated.

After the initial detection of water, several other molecules such as OCS, $HC\equiv C{-}C\equiv N$ and H_2CO were readily detected on the basis of their known laboratory microwave spectra. During

TABLE 1. REPORTED INTERSTELLAR MOLECULES LISTED IN ORDER BY NUMBER OF ATOMS

2	3	4	5	6	7	8	9	10	11	13
H_2	H_2O	H_2CO	H_2C_2O	$HCONH_2$	HC_5N	$HCOOCH_3$	HC_7N	CH_3C_5N	HC_9N	$HC_{11}N$
CH	H_2S	H_2CS	H_2CNH	CH_3CN	$HCOCH_3$	CH_3C_3N	$(CH_3)_2O$	CH_3COCH_3		
CH^+	HCN	$HCNH^+$	H_2NCN	$[CH_3NC]$	CH_3C_2H		CH_3CH_2CN			
C_2	HNC	HNCO	HC_3N	CH_3OH	CH_2CHCN		CH_3CH_2OH			
CN	HCO	HNCS	HCOOH	CH_3SH	NH_2CH_3		CH_3C_4H			
CO	HCO^+	$HOCO^+$	C_3H_2	C_5H	C_6H					
CS	$[HOC^+]$	C_3H	C_4H							
NO	HCS^+	C_3N	SiH_4							
NS	[HNO]	C_3O	CH_4							
OH	N_2H^+	C_3S								
SiO	C_2H	NH_3								
SiS	OCS	H_3O^+								
SO	SO_2	C_2H_2								
SO^+	SiC_2	C_2H_4								
HCl	C_2S									
PN]	[NaOH]									
	$[H_3^+]$									

these initial searches some strong lines, which could not be assigned to any known molecules were occasionally detected. It was not long, however, before Klemperer (1970) made the perceptive conjecture that one of these unassigned (U) lines might belong to the molecular ion HCO^+, protonated CO. This conjecture was subsequently confirmed by Woods *et al.* (1975) who were able to identify the species in a laboratory discharge using the interstellar frequency as a guide. Numerous other well-known small or moderate sized molecules, including a few more unstable species have subsequently been detected. Over 70 molecules are now known, together with estimates of relative abundances, temperatures and an understanding of the molecular composition of numerous astronomical objects. An up-to-date list is given in table 1 (Snyder 1985).

Galactic sites where molecules are found

It is useful to describe briefly a few representative objects in which molecules have been detected (Kroto 1981).

Giant molecular clouds

Part of the Orion Molecular Cloud, OMC1 which is a long cigar-shaped giant molecular cloud, some 100 light years long and 10 light years wide, stretches almost from the central star in Orion's belt (ε Ori) to the star at Orion's left foot (κ Ori). It has become one of the most important regions for detecting new molecules. The region that lies behind the famous Orion emission nebula has become the focus of many studies of the gas dynamics. The results show that this is a site of active star formation.

Cold molecular clouds

There are many small cold molecular clouds which contain molecules. A small dark cloud in Taurus known as TMC1 is one such object. As interesting as any other observation in TMC1 is the fact that this cloud contains an intriguingly large abundance of polyynes, molecules which are essential long chains of carbon atoms. In fact this cloud is extremely cold, *ca.* 5 K, and very quiet with relative molecular velocities of *ca.* 0.1 km s^{-1}, which give rise to radio line widths of *ca.* 10 kHz at 10 GHz.

Cool carbon stars

The third class of object that is important in the context of this paper contains the carbon-rich red giants. The infrared star IRC+10216 is a particularly interesting object that has been studied by both radio and infrared techniques. It is surrounded by a dense shell composed of dust and gas which is expanding at approximately 15–17 km s^{-1}. Another object which is important is the famous variable R Cor Borealis which appears to be releasing puffs of dust at intervals which causes the periodic variations in the magnitude. Loreta (1934) originally suggested that such particles might be forming and O'Keefe (1939) showed that the physico-chemical conditions were such that the grains were probably carbonaceous and driven out into the general interstellar medium by radiation pressure. These types of object now appear to play a key role in the interstellar grain scenario. Further, other important sites are discussed by Duley & Williams (1984).

INTERSTELLAR AND CIRCUMSTELLAR CARBON

Among the first molecules to be observed in the interstellar medium were such species as H—C≡N and H—C≡C—C≡N (HC_nN with n odd and, in this case, equal to 1 and 3). This is because their laboratory microwave spectra were well characterized and their large dipole moments gave rise to very strong radio signals. At about the same time as these early measurements were made the next member of this series, the molecule cyanobutadiyne H—C≡C—C≡C—C≡N (or HC_5N) was synthesized and its laboratory microwave spectrum measured (Alexander *et al.* 1976). These data enabled the radio detection of this species to be made (Avery *et al.* 1976). This detection was a somewhat surprising result at the time as the molecule had six heavy (i.e. non-hydrogen) atoms, two more than any other molecule previously detected. Indeed the strength of the line was such that it clearly broke a rough rule that had gained a degree of acceptance for predicting likely abundances of interstellar molecules. The rule suggested that abundance decreased rapidly with the number of heavy atoms and in particular it appeared that each additional heavy atom tended to reduce the abundance by an order of magnitude.

The next molecule in the series, HC_7N, was then synthesized and its laboratory spectrum measured, figure 1 (Kirby *et al.* 1980), specially to enable the radio search for this species to be made. The subsequent search was immediately successful (Kroto *et al.* 1978; Kroto 1986) in that the species was readily detected in the cold molecular cloud TMC1 (figure 2). Subsequently the next member, HC_9N, was also detected (Broten *et al.* 1978) without the aid of a laboratory measurement. This time a neat extrapolation technique, developed by Oka (1978), was used which predicted very accurately the HC_9N frequencies on the basis of the known values for HC_nN ($n = 1, 3, 5, 7$). Since then $HC_{11}N$ has been detected by using the same procedure (Bell *et al.* 1982).

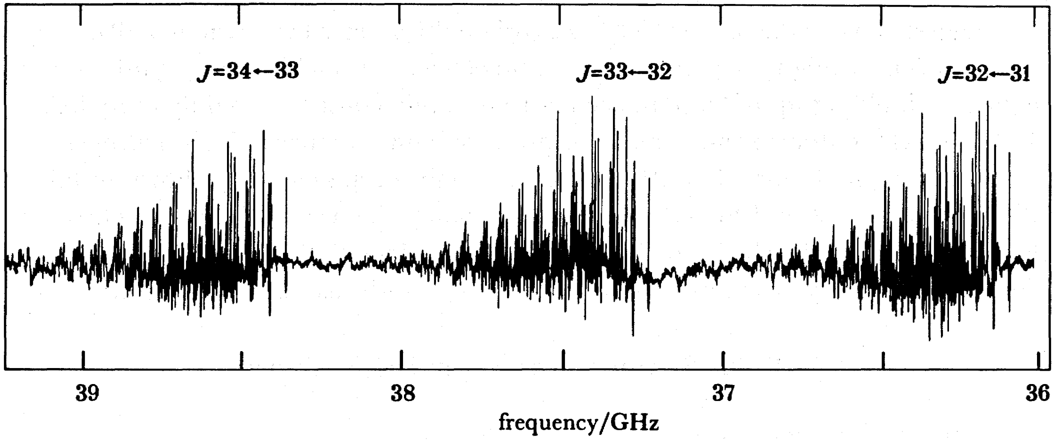

FIGURE 1. The laboratory microwave spectrum of HC_7N (H—C≡C—C≡C—C≡C—C≡N). There are three groups of lines depicted here. The lines at the right-hand end of each group give the radio frequencies of the cold molecule and correspond to those detectable in space.

It was soon found that one of the best places for the detection of carbon chains was the cold cloud TMC 1, however, as more and more molecular sources were discovered it became clear that the remarkable late N-type carbon-rich supergiant IRC+10216 also contained very high

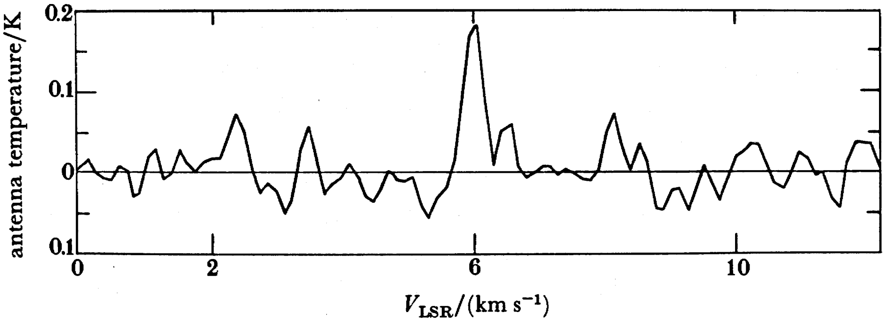

FIGURE 2. The radio line of HC_7N detected on the basis of the measurements of the lines given in figure 1. $J = 21 \rightarrow 20$, cloud 2.

abundance of the cyanopolyynes. Indeed apart from the polyynes, several other interesting carbon chain molecules have been detected in this object. These are the radicals C_3N and C_4H (Guélin & Thaddeus 1977; Guélin *et al.* 1978) and more recently Cernicharo *et al.* 1986 Guélin *et al.*, 1987) have detected the species C_5H and C_6H. These observations suggest that there are interesting similarities between the molecular compositions of TMC1 and IRC+10216 which really need to be understood.

The detection of these somewhat exotic species posed a number of questions. The first one that was suggested when the species HC_5N was originally detected was whether all other related molecular analogues might be present. This seemed very reasonable as any synthesis involving the sequential building up of large molecules from a mix consisting mainly of hydrogen with *ca.* 0.001 % C/N/O atoms seemed likely to produce highly reduced (high hydrogen content) carbon-containing molecules. For HC_3N there are only 14 analogues as shown in table 2 but for HC_5N there are 72 and for $HC_{11}N$ there are 8992 (August *et al.* 1986). These are only simple analogues; if branched carbon chains are considered there will be many more. In addition, the possibility of the associated ions and free radicals needs to be considered.

TABLE 2. MOLECULES IN THE HC_3N FAMILY

HC_3N	$HC\equiv C-C\equiv N$[a]			1
H_3C_3N	$CH_2=CH-C\equiv N$[a]	$HC\equiv C-CH=NH$	$CH_2=C=C=NH$	3
H_5C_3N	$CH_2=CH-CH=NH$	$CH_3CH=C=NH$	$CH_2=C=CHNH_2$	6
	$HC\equiv C-CH_2NH_2$	$CH_3C\equiv CNH_2$	$CH_3CH_2C\equiv N$[a]	
H_7C_3N	$CH_2=CH-CH_2NH_2$	$CH_3CH=CH-NH_2$	$CH_3CH_2CH=NH$	3
H_9C_3N	$CH_3CH_2CH_2NH_2$			1

Experiments have been done which aimed at answering the question of whether the related species are present or not. Searches for $H-C\equiv C-CH\equiv NH$ (Kroto & Little 1988) (figure 3) and $CH_2=CH-C\equiv C-C\equiv N$ (Kroto *et al.* 1985) have yielded upper limits for the abundances of these species. These studies have shown that as a chain with a given number of carbon atoms adds sequentially more H the relative abundance drops rapidly. Of course it must be remembered that these species are significantly more difficult to detect (Kroto 1981). However, notwithstanding this it really does seem as though the numerous feasible hydrocarbon relatives are essentially absent. It is possible that there is an as yet unidentifed chemistry that pref-

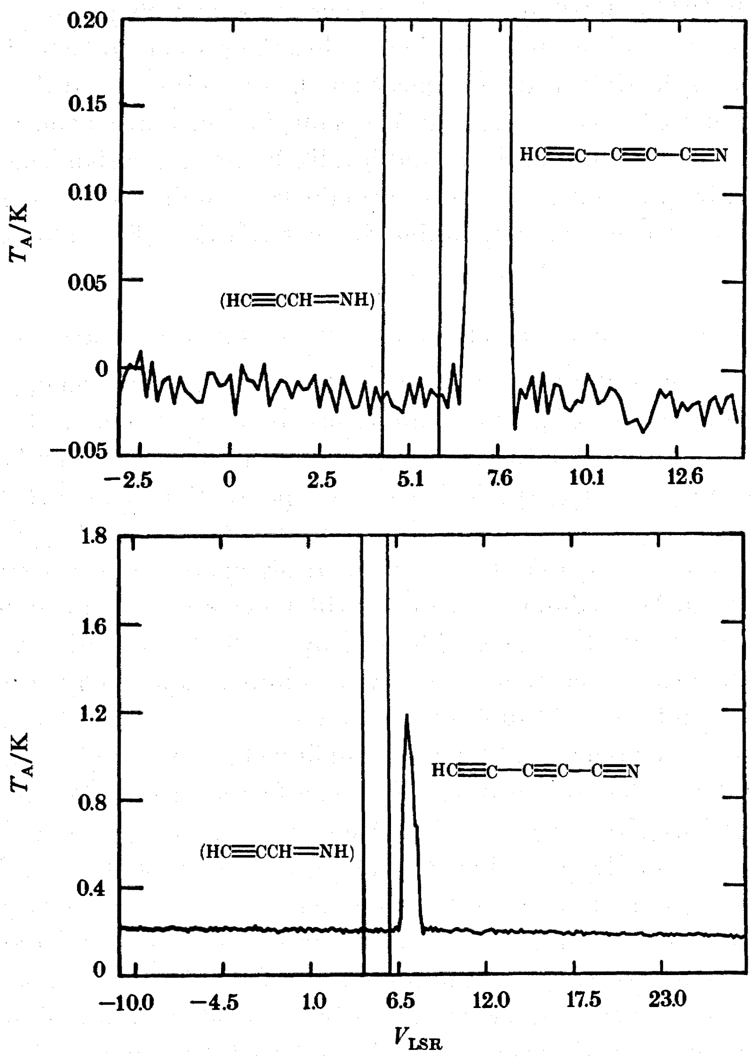

FIGURE 3. The result of a radio search for HC≡C—CH≡NH. The upper trace is a × 8 enlargement of the lower trace. The strong line belongs to HC_5N and the line being searched for should lie between the vertical bar lines.

erentially leads to the formation of the long chains. At present the most successful theories of interstellar molecule formation are based on the ion-molecule schemes of Herbst & Klemperer (1973), Dalgarno & Black (1976), Watson (1976, 1978) and Duley & Williams (1984). These together with laboratory experiments such as those of Smith & Adams (1981) have been very successful in explaining the abundances of many of the smaller molecules that have been detected. However, the cyanopolyynes do present a problem as it is not at all clear that such processes can give only the polyynes in the absence of all the other closely related species. It is of course possible that these species are produced and that they are readily fragmented to the more stable polyynes and this possibility should not be overlooked. However, another alternative scenario involving carbon stars seems to present a much more likely possibility.

As noted previously, an interesting aspect of the polyyne detection is that they are found to be very abundant in two specific objects, TMC1 and IRC+10216, both of which have very low ion abundances, indeed no ions have so far been detected in IRC+10216. Secondly, the infrared luminosity of IRC+10216 is variable because it is pumping grains, presumably carbonaceous, into the general interstellar medium. Thus there seems to be an intimate link between the formation of the dust in the circumstellar shell of this star and the long carbon chain molecules. A circumstellar scenario appears to operate in which carbon atoms synthesized in the star can nucleate to form dust particles and it is likely that the carbon chains are some forms of intermediates, by-products or breakdown products or all three of these at once. This process is likely to be related to that responsible for soot (Kroto 1981, 1982; Zhang *et al.* 1986).

LABORATORY STUDIES OF THE CARBON NUCLEATION PROCESS

There have been many interesting experiments that have focused attention on the nature of carbon in the vapour phase. One of the most interesting from an astrophysical point of view was the work of Douglas (1951) who was able to show that the 4050 Å† comet band was due to C_3, a species that with C_2 is a major species in carbon vapour. Hintenberger *et al.* (1963) did very interesting mass-spectrometric measurements that indicated that much larger species, with as many as 33 carbon atoms, are produced in a carbon arc discharge. Our discovery of the long carbon chains in the interstellar medium, when linked with these results suggested the intriguing possibility that there might even be chains with as many as 33 atoms floating around in the interstellar medium. It thus seemed that some new laboratory experiments were called for which aimed at a close study of the nature of the large carbon species produced by carbon vaporization. Such a study also offered the further possibility of a clearer understanding of both the origin of chains and carbon grains as it was beginning to appear that the two were linked in some symbiotic relation (Kroto 1981, 1982). Another intriguing prospect that Douglas (1977) suggested, which certainly merited consideration, was the possibility that long carbon chain modecules might be responsible for the diffuse interstellar features (Herbig 1975).

Recent experimental advances have allowed the clusters of refractory materials to be produced and studied (Hopkins *et al.* 1983). The technique was first applied to carbon by Rohlfing *et al.* (1984) who were able to show that there was a second even larger family of carbon clusters than had previously been detected. They were able to detect even-numbered aggregates of carbon atoms with from 30 to 190 atoms. This technique seemed to offer an ideal method for mimicking the processes that obtain in the circumstellar shell of a carbon star. Not only could the carbon clustering process be studied in the presence of hydrogen and other gases that occur in circumstellar shells but the technique also offered the possibility of checking whether chains had spectra consistent with the diffuse interstellar features. One of the results of this experiment is shown in figure 4, which shows the mass spectrum produced when carbon is allowed to cluster under high-pressure conditions. There are a number of interesting observations to be made on this result. The relative intensities of the peaks in the region below C_{30} are more or less the same as was observed originally by Hintenberger *et al.* (1963). The specrum above C_{30} is, however, strikingly different from that of Rohlfing *et al.* (1984) in that the peaks at C_{60} and to a lesser extent C_{70} are an order of magnitude stronger than those nearby.

Two sets of experiments were carried out which probed the behaviour of the carbon clusters. The first set probed the chemical reactivity of the smaller clusters to see whether they behave like relatives of the interstellar cyanopolyynes, HC_nN. Reactions with gases which could lead

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† 1 Å = 10^{-1} nm = 10^{-10} m.

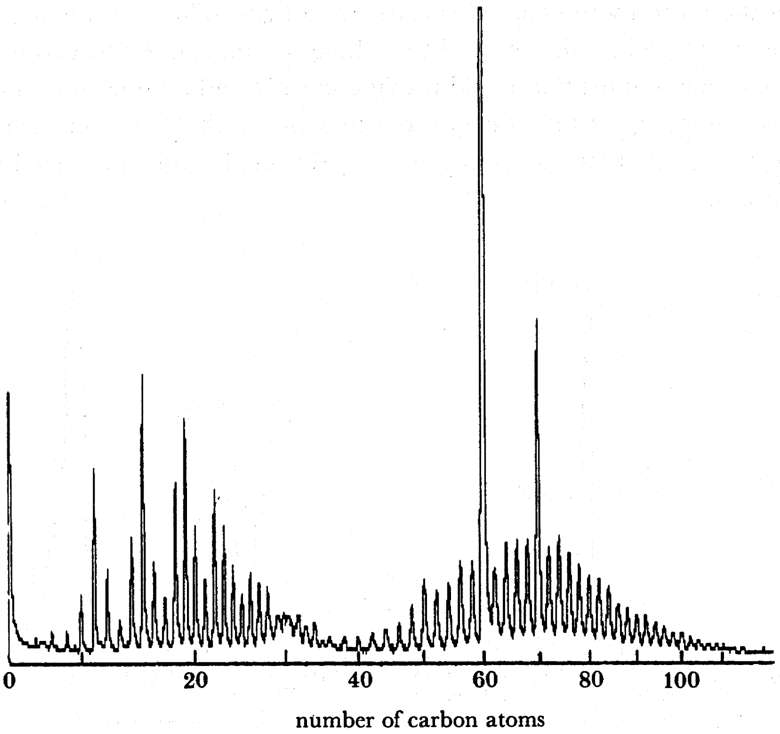


FIGURE 4. Mass spectrum of carbon clusters under conditions where a moderate amount of nucleation has occurred.

to the introduction of H and N into the species were studied (Heath *et al.* 1987; Kroto *et al.* 1987). The results of one such experiment that uses admixed water are shown in figure 5. Here we see that when small quantities of water are introduced into the system the even clusters immediately add two H atoms. This result is perfectly explicable if the species are linear chains. Indeed the results suggest that chains of up to 20 or more carbon atoms are feasible. Under

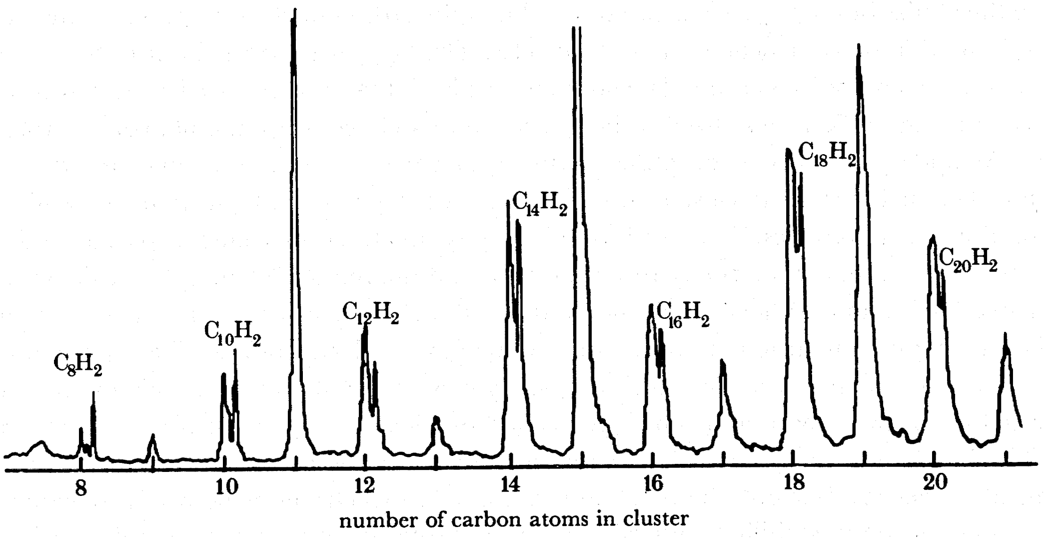


FIGURE 5. Mass spectrum of carbon clusters produced in the presence of water vapour. Each even cluster has grown a satellite at +2 mass units consistent with the formation of H—(C≡C)$_n$—H linear species.

these conditions the more hydrogenated species are absent. These results are consistent with those of Rohlfing *et al.* (1984) who showed that these species could add two potassium atoms. The experiments with reactants that could provide both H and N showed that it was relatively easy to form the cyanopolyynes under conditions in which carbon clusters form in the presence of H and N atoms. In particular the species actually detected can be produced relatively easily as shown in figure 6.

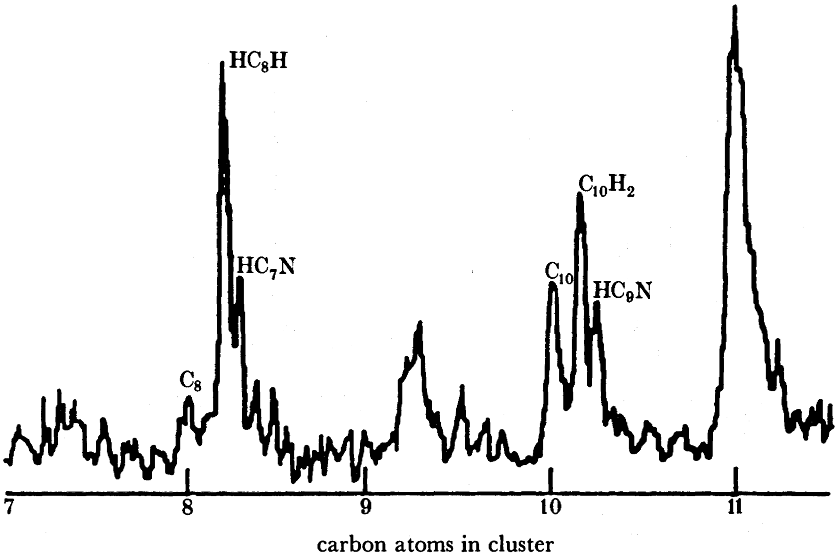


FIGURE 6. Mass spectrum of carbon clusters produced in the presence of hydrogen and nitrogen showing peaks consistent with the formation of the known interstellar species HC_7N and HC_9N.

The second set of experiments, which had not been anticipated, aimed to probe the reason for the remarkable dominance of the peak at for the 60 carbon cluster. After a few experiments it became clear that it was possible to produce conditions in which essentially only C_{60} and C_{70} were readily detectable, figure 7. This was achieved by allowing the clustering process to continue for significant periods. It ultimately became clear that these remarkable results were due to the ability of the C_{60} cluster to survive the rapid carbon nucleation process which results in the formation of macroscopic carbon particles. The C_{60} cluster turned out to be unreactive and stable to photodissociation. It was then realized that the properties that this species displayed could all be rationalized if the species were a closed graphitic network (Kroto *et al.* 1985). An open or flat sheet of graphite would be extremely reactive at its edges and this species was not. For such a sheet to close it is necessary for pentagonal configurations to be dispersed among the hexagonal ones. As a result, the highly symmetrical molecule displayed in figure 8 was proposed (Kroto *et al.* 1985) to account for the dominance of the C_{60} peak. It has 12 pentagonal faces and 20 hexagonal ones and has the truncated icosahedral symmetry which has become most familiar to us in the construction of the modern football. That such a molecule might actually *form spontaneously* was a completely new proposal although such a structure was discussed by Osawa (1970) and Jones (1966) had previously made an inspired suggestion that it might be possible to close carbon networks. Such a structure has a number of exciting chemical properties. It should be very stable as far as the electronic structure is concerned and also possess geodetic stability. Indeed this latter property was such a significant factor in arriving at a possible structure that the molecule was named buckminsterfullerene after the

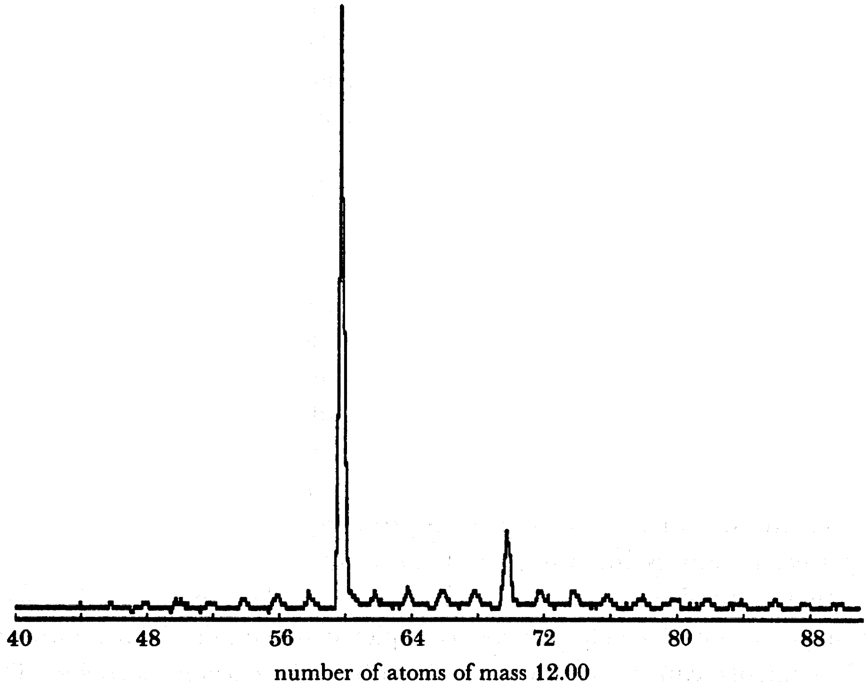


FIGURE 7. Mass spectrum obtained under clustering conditions which dramatically show the peaks for C_{60} and, to a lesser extent, C_{70} to be dominant.

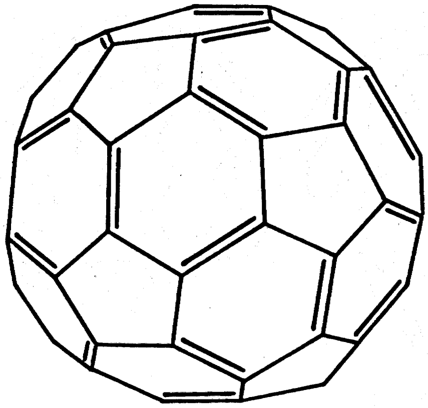
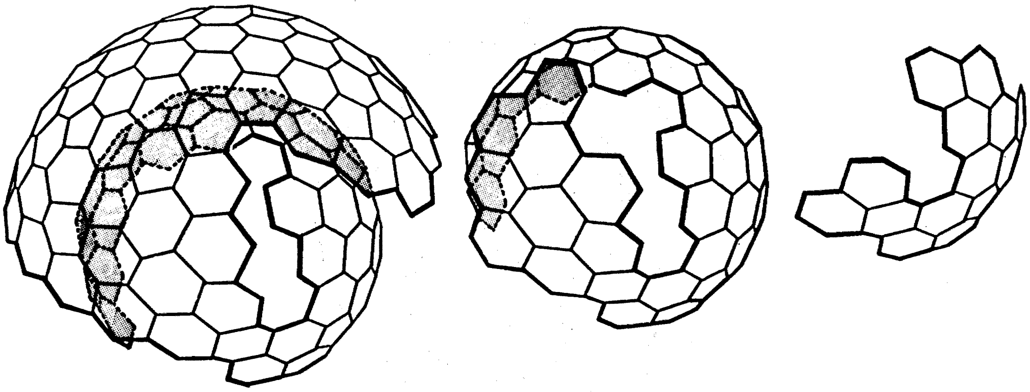


FIGURE 8. The truncated icosahedral structure proposed to account for the stability of the C_{60} molecule.

designer of the geodetic domes that are now universally used for efficiently enclosing large spaces as in the case of radomes and the Epcot centre in Florida (Buckminster Fuller 1983). There are other pieces of evidence that substantiate the proposal that closed cages are formed during carbon nucleation. For instance, closure necessitates the inclusion of twelve pentagonal configurations by Euler's rules though the number of hexagonal ones is arbitrary. It has been proposed that the pentagons should be completely isolated by hexagons for stable closed configurations in which there is optimum fulfilment of chemical and geodesic requirements (Kroto 1987). On this basis C_{60} is the first outstanding contender as it is the smallest cage that can fulfil this proviso and although it is not obvious, C_{70} is the next larger cage able to do so similarly (Kroto 1987; Schmalz *et al.* 1988). This is clearly consistent with the experimental results shown in figure 8. Further refinement of these ideas leads to the prediction that there are other so-called magic numbers for C_{50}, C_{36}, C_{32} and C_{28} (Kroto 1987). These species also show significant extra degrees of relative stability under certain conditions (Heath *et al.* 1988).

Perhaps the most important aspect of this discovery is the fact that such structures form spontaneously. It was this realization that resulted in a beautifully simple picture of the nucleation step (Zhang *et al.* 1986; Kroto 1986; Heath *et al.* 1988). The proposed mechanism has as its key element the fact that a flat graphitic network with a few tens of atoms or so will be unstable relative to one which has eliminated dangling bonds at the edge atoms by curling up, most effectively so of course in the case of perfect closure. To curl and close, pentagonal configurations must be dispersed among the hexagonal ones, as a sheet consisting only of hexagonal configurations cannot close (Thompson 1942). It is likely that the vast majority of the clusters will be only partly closed and indeed most will probably be species in which the edges missed closure and in fact overlap of the trailing edge has occurred, figure 9. Once overlapped, perfect closure is impossible and the result will be rapid growth rather like a snowball accreting a complex continuous layer network, broken occasionally at various points to allow multilayer formation. The process is depicted schematically in figure 9 where the various small segments can be considered as embryonic carbon particles. The ultimate structures are expected to be onion-like, spheroidal particles in which the interlayer spacing is *ca.* 3.4 Å as in graphite.



It is clear that the pentagonal configurations, which are crucial features of the general nucleation process, occasionally will occur at just the correct places for closure to be feasible. Such closed species will have ended in a cul-de-sac unable to grow beyond this stage. The species will be left behind as the majority carry on to form large particles. Such particles are too large for detection by the mass spectrometer used to obtain the spectrum shown in figure 3 and as a consequence only C_{60} and C_{70} appear to be present.

As a further justification of the process proposed here we can note that spheroidal particles with exactly this type of structure have been observed by Iijima (1980) and one example is shown in figure 10.

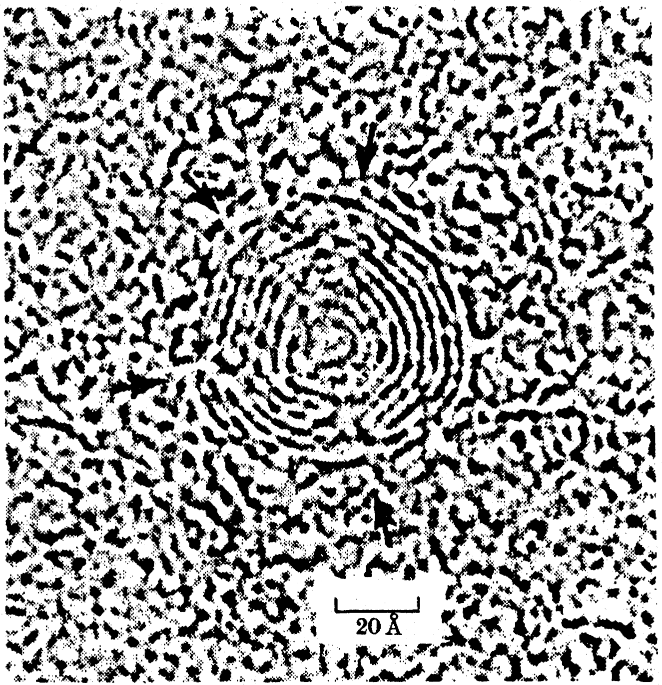


FIGURE 10. Transmission electron microscope picture of a spheroidal partical detected by Iijima (1980). The spacing between the layers is very close to the graphite interlayer spacing.

CONCLUSIONS

The discovery of long-carbon-chain molecules in the interstellar medium has led to the discovery that when carbon vapour nucleates in the vapour phase not only do the chains form spontaneously but so also do large carbon particles and such molecules as C_{60}. That closed carbon networks also can form spontaneously heralds an entirely new perspective on a wide range of chemical problems involving that most mercurial of elements, carbon. It has opened up the way to an understanding of how soot forms in combustion, a process of fundamental economic importance. In addition, it implies the existence of a chemistry that exploits the fact that, in the gas phase, curved graphitic carbon networks form rather than the flat graphitic ones as has long been taken for granted.

The new ranges of compounds heralded by C_{60} itself and its $C_{60}M$ complexes (Heath *et al.* 1985) are not only exciting from a theoretical standpoint but also from a practical one as the compounds are likely to posses unique chemical and physical properties. Perhaps as intriguing as any other aspect of the discovery are the astrophysical implications. Wherever carbon forms macroscopic particles in the gas phase, and it appears to do so ubiquitously in the Universe, a remarkably stable C_{60} molecule also forms, whatever its structure! Thus it is quite conceivable that significant quantities of this species are distributed throughout interstellar space. If the preliminary observations on its resilience, particularly to photolysis (Heath *et al.* 1985), are correct then it could be the most widespread molecule in space, perhaps more able to withstand destruction by the harsh ambient starlight flux than any other molecule. It is likely that the ion is the dominant species in the regions of low shielding from starlight.

Perhaps as important as anything else is the fact that the structure of C_{60} has, almost inadvertently, provided a key to the morphology and mechanism of formation of macroscopic carbon particles both on earth in combustion processes and in circumstellar dust formation. Thus we now have a candidate for the missing link, the embryo which is the site of the fundamental accretion process that leads not just to an interstellar or circumstellar grain but perhaps more significantly the ultimate accretion objects, stars and planets.

It is a pleasure to acknowledge the contributions of Lorne Avery, Norm Broten, Bob Curl, James Heath, Colin Kirby, Lesley Little, John MacLeod, Don McNaughton, Sean O'Brien, Osman I. Osman, Takeshi Oka, Rick Smalley, Nenad Trinajstic and David Walton to the various research programmes surveyed here.

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Note added in proof (2 *November* 1987). Since this article was written there have been some interesting developments relating to the formation and structure of carbonaceous particles, which are of importance as far as interstellar and circumstellar dust are concerned. The hypothetical nucleation mechanism shown schematically in figure 9 has been studied in more detail by molecular modelling as a preliminary to computer simulation studies (Kroto & McKay 1988). As discussed previously, if we assume that carbon nucleation is an energy-driven process, then curved rather than flat graphitic sheets will be the intermediates in carbon particle formation and C_{60} is a highly probable by-product. With some important refinements the structural properties of the resulting particles can be predicted (Kroto & McKay 1987). In the nucleation scenario, a growing embryonic network should have bond lengths and angles consistent with those of an extended polyaromatic hydrocarbon ring system in which isolated corannulene segments play a key role. As the shell-like structure grows larger, the shape should take on the characteristics of a large cage. Such cages have been constructed as shown in figure 11 and they exhibit an important effect in that the relatively round shape of the small

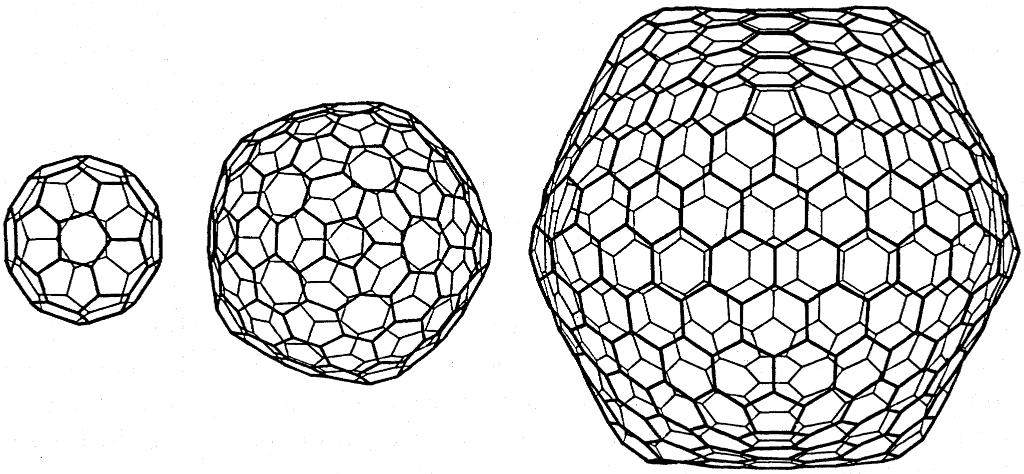

FIGURE 11. A set of models for the closed symmetric fullerenes C_{60}, C_{240} and C_{540}. The diameters of the latter cages are two and three times that of C_{60}. The rapid shift towards quasi-icosahedral symmetry is quite striking.

cages, such as the C_{60} truncated icosahedron, changes as the cage diameter increases and flat faces develop very rapidly. As the size increases the 12 pentagonal truncation points become localized at fairly sharp cusps in the surface and a quasi-icosahedral shape, with 20 more-or-less flat triangular planes which fold smoothly into each other, develops. A crucial refinement in the spiral growth mechanism must be introduced; for optimal growth, fresh network will form at an altitude of *ca.* 3.4–3.5 Å above the previous layer and this can be achieved most readily by locating the twelve necessary and sufficient pentagons in each full turn of the spiral directly over those in the immediately previous segment. This epitaxial growth pattern will result in a single particle with three-dimensional structural integrity. The pentagons will be located along twelve radii resulting essentially in a spiral single crystal consisting effectively of 20 pyramidal microcrystallite components. The flat hexagonal layers, out of which any one microcrystallite is formed, fold into the layers of the microcrystallites which adjoin it on three of its faces. There will of course be some discontinuities in the spiral. As the contour of a large cage shows quasi-icosahedral shape, in cross-section a large particle should appear roughly as a spiral maze whose walls have straight sections curving smoothly into each other to exhibit a polygonal shape. In figure 12 one of Iijima's (1980) particles is shown which at first sight appears to be spheroidal. Under close scrutiny, however, it is seen to consist of concentric polyhedral shells in excellent agreement with the model.

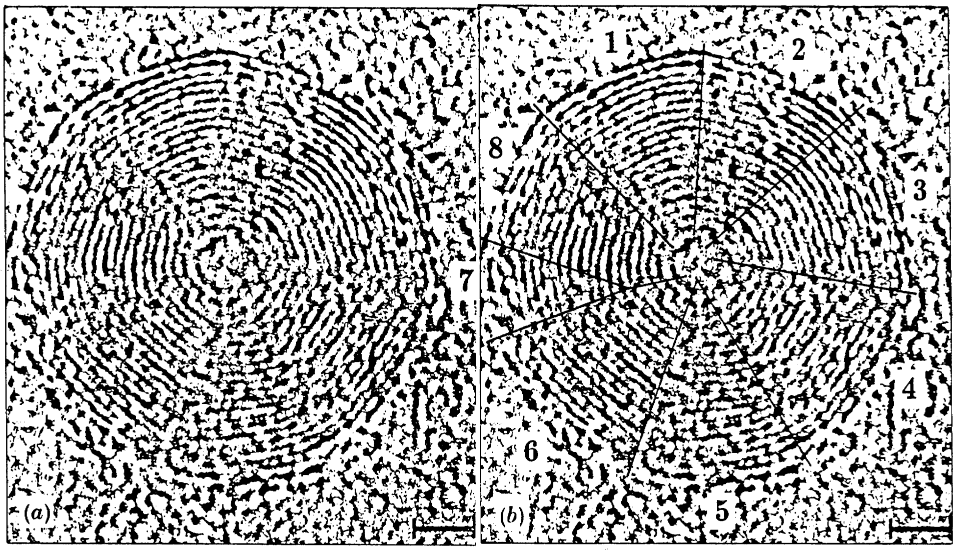

FIGURE 12. (*a*) Contrast enhanced image of a transmission electron micrograph published by Iijima (1980) and (*b*) the same image is marked to delineate the features which appear to be consistent with pyramidal layered microcrystallite cross sections predicted by the carbon nucleation growth scheme.

A second important observation has very recently been made and this is the observation by Gerhardt *et al.* (1987) that C_{60}^{+} is the dominant ion in a sooting flame. This observation is very good support for the proposal that the nucleation mechanism is not only correct but that it has widespread applicability in that carbon cages also occur in the presence of hydrogen if the physicochemical conditions are right, i.e. during soot-formation.

Recently there has also been an interesting radio observation by Rieu *et al.* (1986). They have shown that in the Egg Nebula (CRL2688) the central object is surrounded by a small ammonia cloud which lies more-or-less *within* a dusty envelope which can be seen optically. Most interestingly, however, is their further observation that just *outside* the dusty region is a second larger extended molecular cloud in which significant quantities of cyanopolyyne chains are detected. It is tempting to explain the formation of the chains as starlight photofragmentation products from the outer regions of a large carbonaceous dust cloud and that the presently visible cloud is an inner remnant, soon to be destroyed.

These observations can be summarized as follows: carbon chains and grains are indeed intimately related and it appears that the chains can be formed by breakdown of carbon particles. They also appear to be intermediates in carbon particle formation as well. The evidence suggests that any dust that is associated with carbon chain molecules must be very similar in constitution to the particles formed in terrestrial carbon nucleation processes. In this case the particles are likely to be shell-like structures consisting of graphitic networks of concentric spiral polyhedral segments. Perhaps the most interesting conclusion relates to the discovery of the third character in the relation. In the experiments done in the laboratory we find that whenever chains and carbon particles form so also does C_{60} and, what is more, this molecule is exceptionally resistant to chemical attack and to photofragmentation Thus in regions such as the outer reaches of the Egg Nebula our knowledge points unequivocally to the distinct possibility that C_{60} is also present. This molecule is unique in that it should be the last survivor in the chaotic processes involved in primordial particle formation and destruction and thus should have a ubiquitous presence in space. It is thus also tempting to conjecture as to whether it is responsible, probably as the ion C_{60}^+, for some of the diffuse interstellar features and perhaps some of the unidentified infrared lines. It certainly seems very likely that partly hydrogenated spiral particles related to the objects considered here will have infrared emission features similar to those of polyaromatic hydrocarbons which have been suggested as carriers of the unidentified infrared bands (Leger & Puget 1984).

It is satisfying to note that some fairly simple concepts now allow many aspects of interstellar and circumstellar carbon chemistry to fall neatly into place.

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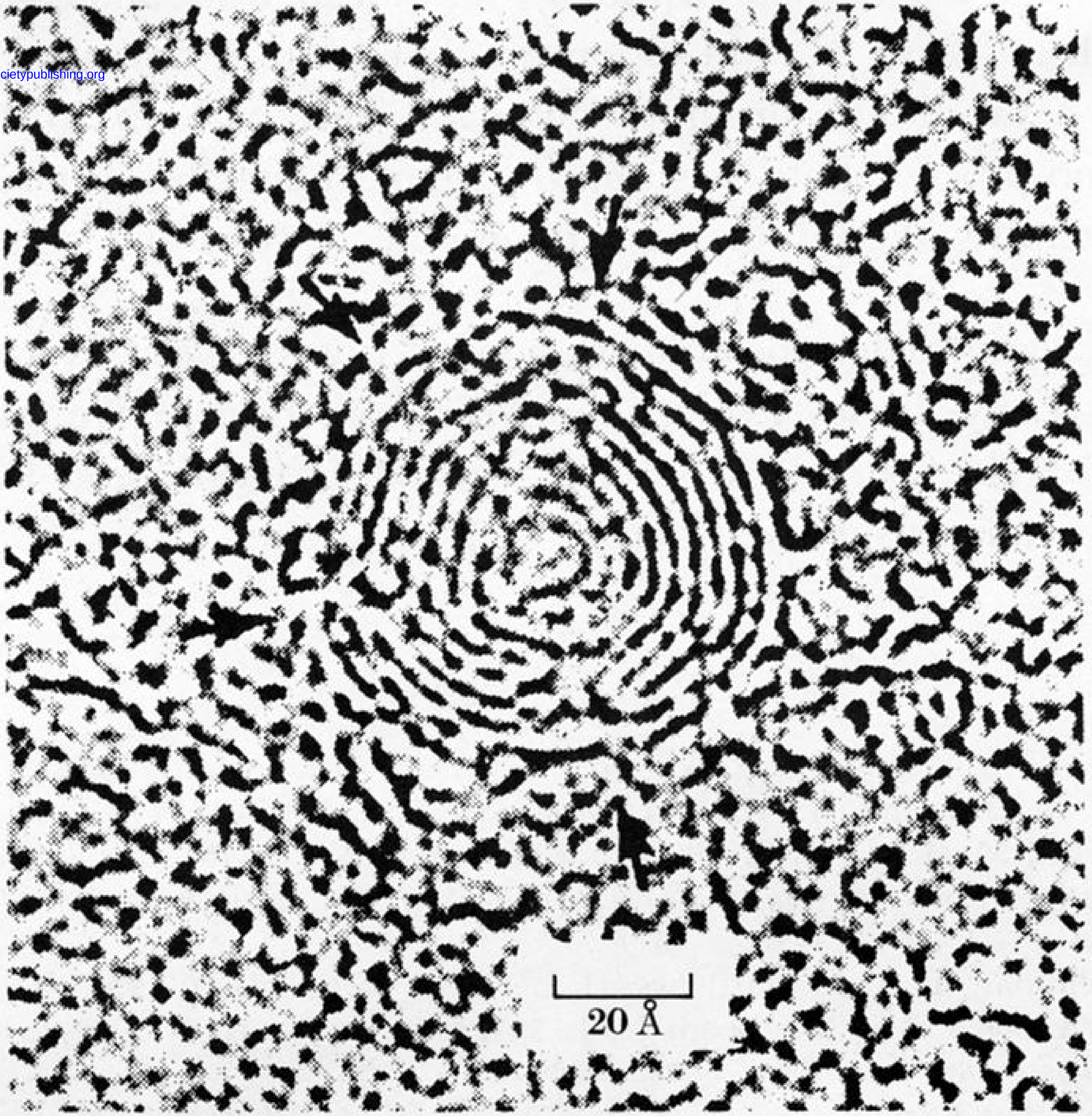

IGURE 10. Transmission electron microscope picture of a spheroidal partical detected by Iijima (1980). The spacing between the layers is very close to the graphite interlayer spacing.

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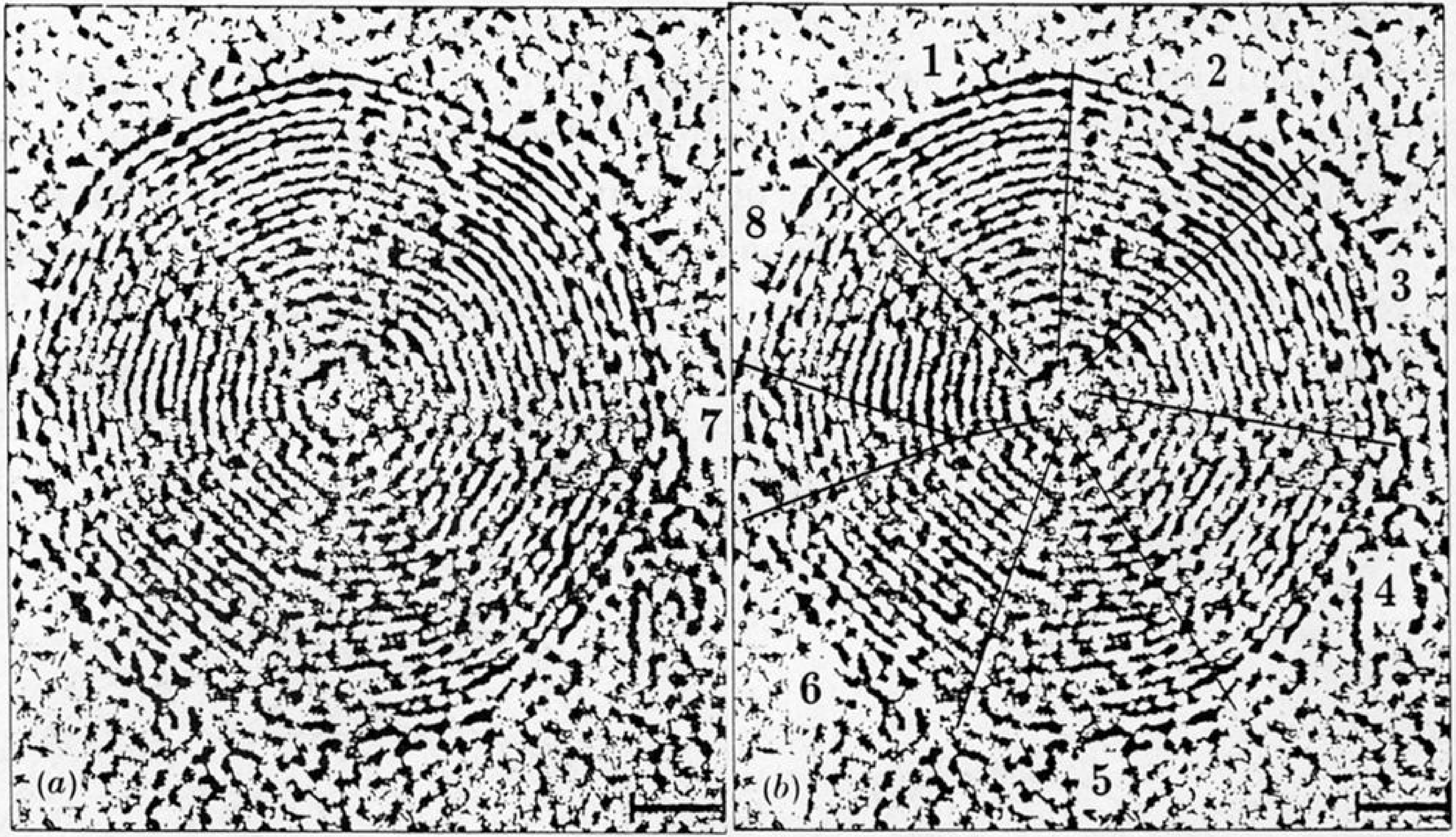

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