

Astro2020 Science White Paper

Lifting the Veil on Aromatic Chemistry: Complex Carbon Across the Stellar Life Cycle from Birth to the Afterlife

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Abstract (optional): In the last several years, significant advances in our knowledge of complex chemical inventories have revealed that there may be a substantial reservoir of undetected carbon present and influencing the star and planet-formation process from the very earliest stages. Here, we outline the observational, laboratory, and modeling needs to explore and understand the potentially critical role that aromatic molecules may play. The continued support of the Green Bank Telescope, as well as the upcoming JWST and planned ngVLA will be crucial to the observational success of this work. The community must also support dedicated teams of laboratory astrophysicists and astrochemical modelers whose work is essential to the proper interpretation of observational results.

Less than 70 years have passed since the discovery of the first interstellar molecule, CH (McKellar 1940). As the field moves toward more complex chemistry, we are now exploring the full life cycle of interstellar chemistry from the birth of stars (McGuire et al. 2018) to the delivery of material to nascent planetary systems (Cleeves et al. 2014) to its re-injection after stellar death (Cami et al. 2010). Yet, the previously fertile hunting grounds for new molecules (Sgr B2(N) and Orion-KL) are rapidly becoming too line-confusion limited at mm-wavelengths to unambiguously make many new detections, even leveraging the power of ALMA to spatially disentangle the emission. Indeed, the extreme complexity of the physical environments in these sources continue to make even the most dedicated attempts to model the chemistry challenging (Garrod 2013). Further, the chemical make-up of these sources is biasing new molecular detections toward saturated molecules at the late stages of chemical evolution, leaving a gap in our understanding of the unsaturated inventory of molecules that dominate at early stages of star formation and chemical evolution.

Pre-collapse dense, dark clouds such as TMC-1 have long been a source of new molecular detections, particularly of unsaturated¹ carbon-chain species that are far less abundant relative to complex organic molecules in prototypical hot core sources such as Sgr B2(N) and Orion-KL (see, e.g., Kaifu et al. 2004; Saito et al. 1987). The extremely narrow linewidths associated with cold cores (~ 0.4 km/s for TMC-1) make high-sensitivity observations across a broad bandwidth challenging. Indeed, the largest such survey was conducted by Kaifu et al. (2004) from 8.8 – 50 GHz using data collected over more than a decade with the Nobeyama 45 m telescope. The survey produced 11 new molecular detections, among other scientific insights. Yet, the ultimate noise level was quite high (~ 10 mK), and the achievable velocity resolution (0.22 – 1.26 km/s across the survey) meant that many spectral lines were convolved into only one or two channels, complicating or even precluding the detection of new species.

We have recently reported the detection of benzonitrile (BN; C_6H_5CN ; Fig. 1) in TMC-1 using extremely sensitive (2 mK), high-resolution (0.05 km s⁻¹) observations of TMC-1 with the 100 m Green Bank Telescope (McGuire et al. 2018). BN is the largest and most chemically and structurally complex molecule ever detected with radio astronomy, and its presence at the very earliest stages of star-formation stands in striking contrast to other complex molecules which are nearly exclusively found in active, high-mass star-forming regions (McGuire 2018). At the other end of the evolutionary spectrum, the fullerene species, namely C_{60} and C_{70} , are found prominently in planetary nebulae and other end-of-life stellar environments (Cami et al. 2010). And in between, in nearly every reasonable galactic and extragalactic environment with sufficient UV fields to drive a detectable fluorescence emission signal, the polycyclic aromatic hydrocarbons (PAHs) are seen to be ubiquitous and abundant, making up as much as 25% of the interstellar carbon budget while remaining largely enigmatic, defying individual molecular detection (Tielens 2008).

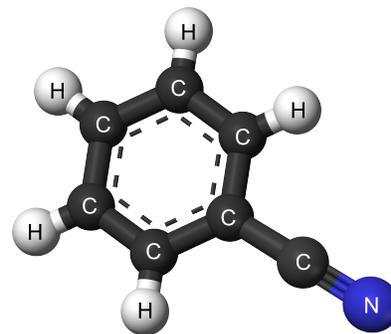


Figure 1: Structure of benzonitrile (C_6H_5CN).

¹Those molecules for which electrons are predominantly bound in forming bonds between heavy elements such as carbon, rather than to bond hydrogen atoms.

These detections, and in particular that of C_6H_5CN , raise important questions that we are only now beginning to be able to ask, and the answers will require dedicated effort over the next decade with extant and new observational facilities:

1. When and how does the first aromatic benzene ring form, upon which all further chemistry driving toward the PAH carbon sink is built?
2. Does the aromatic chemistry seen in the earliest stages of star formation survive the birth of a star, or is the chemistry reset?
3. How does the presence of these large molecules, and this massive sink of interstellar carbon, influence the star formation process, and eventually the formation and carbon content of planets?
4. Is the fullerene and PAH content seen at the end of the stellar life cycle an unbroken link to the earlier molecular cloud, and does it form the basis of the carbon chemistry for the next generation of stars and planets?

In the following pages, we touch upon each of these unanswered questions, and discuss what facilities and resources the community must support to enable us to answer them.

When and how does the first aromatic benzene ring form, upon which all further chemistry driving toward the PAH carbon sink is built?

This question can only be answered by a close collaboration between interstellar observations and laboratory astrophysics experiments. In the last decade, several laboratory efforts have examined the potentially viable pathways to form benzene (C_6H_6) under ISM conditions (see, e.g., [Jones et al. 2011](#)). Yet, the critical precursor species 1,3-butadiene ($H_2CCHCHCH_2$) and C_6H_6 itself are both invisible to radio astronomy, and C_6H_6 has only been detected in a very small handful of environments, requiring space-based infrared observations ([Cernicharo et al. 2001](#)). This makes the interstellar verification and modeling of the pathways studied in the lab extremely challenging. Indeed, no extant facility can observe C_6H_6 , as its detectable transitions are completely obscured by the atmosphere, even from SOFIA, and no space-based facility covers the range at sufficient resolution. **Observations with the James Webb Space Telescope (JWST), and potentially the Origins Space Telescope, in the coming decade will be critical to furthering these investigations of C_6H_6 directly.**

Another option is to use an observational proxy for C_6H_6 . Work by ourselves and others have shown that C_6H_5CN can serve as a direct observational proxy for C_6H_6 ([Lee et al. 2019](#)). The only extant facility in the world capable of reliably observing C_6H_5CN in the ISM, and thus enabling its use to study the chemistry of C_6H_6 , is the 100 m Green Bank Telescope (GBT). There is no other facility planned or extant capable of carrying out these observations in the cold, extended pre-stellar environments. **Observations and study of carbon chemistry in pre-stellar environments relies nearly exclusively on the continued operation of the GBT over the next decade and beyond. Increased support for Open Skies observing on the GBT will substantially benefit these efforts.**

The formation of the PAH carbon-sink is now widely thought to occur through reactions beginning with C_6H_6 , but the exact mechanisms of this formation pathway, especially under interstellar conditions and using interstellar precursors, is a topic of extreme uncertainty (Tielens 2008). Our recent work in the laboratory studying the formation of C_6H_5CN is only the first step in understanding this process (Lee et al. 2019). Expansions of this work to study the formation of the next ring, making naphthalene ($C_{10}H_8$) are only the immediate next step. The microwave spectra of the CN-substituted naphthalenes ($C_{10}H_7CN$) have recently been measured (McNaughton et al. 2018), enabling their use as proxies for naphthalene in the same way BN is a proxy for C_6H_6 , but only if laboratory studies can unravel and quantify the formation mechanisms. **The community must strongly support laboratory efforts in the coming decade to study carbon evolutionary processes and the accompanying microwave spectroscopy necessary to enable their observation in the ISM.**

Does the aromatic chemistry seen in the earliest stages of star formation survive the birth of a star, or is the chemistry reset?

Through recent observations with the GBT, we have definitively detected BN in three additional sources outside TMC-1 (McGuire et al. 2019, in prep.). These sources are all further along the evolutionary pathway than TMC-1, with embedded cores and warmer temperatures. This suggests that BN, and aromatic chemistry, is not a mere chemical curiosity in TMC-1, but is indeed a common and substantial part of the star-formation process. As with the initial detection of BN, these observations are only possible with the GBT, as the emission appears to be spatially extended, weak, and with very narrow spectral linewidths. **Further observations of a wider sample of sources is clearly needed, and can only be accomplished with the GBT.**

Proceeding even further along the evolutionary spectrum to the protostellar phase will almost certainly require a new facility. As collapse proceeds and the natal molecular cloud warms, beam dilution and partition function effects will almost certainly drive the molecular signal to be too weak to be detectable in the relatively large ($\sim 30''$ at 20 GHz) beam of the GBT. No extant facility possesses the correct combination of spatial resolution and surface-brightness sensitivity to accomplish the task. **Observations of aromatic chemistry on the $0.1'' - 3''$ scales of warmer protostellar sources, with the accompanying weaker line emission, will fundamentally require a facility such as the planned Next Generation Very Large Array (ngVLA; Selina et al. 2018).**

How does the presence of these large molecules, and this massive sink of interstellar carbon, influence the star formation process, and eventually the formation and carbon content of planets?

The C/O ratio in planetary atmospheres has been proposed to be not only a useful probe of the history of an exoplanet, but one that is reliably observable with extant and future facilities (Öberg et al. 2011). Effectively using observed exoplanet elemental ratios to test those models therefore relies heavily on our ability to accurately interpret chemical abundances measured in disks to infer the inventory of undetectable species, and how these measurements affect observed elemental ratios. These measurements themselves are extremely challenging, and even with ALMA we are reaching the limits of detectable molecular complexity (Walsh et al. 2014). How, then are we to hope to understand the influence of the potential reservoir of carbon in the form of aromatic

molecules that could have a substantial, and unaccounted for, effect on the measured C/O ratio?

Assuming that aromatic chemistry can be reliably traced from the pre-collapse through protostellar phases using the GBT and ngVLA, we must then rely upon astrochemical models to carry the information forward in time once we lose the observational trail. **It is therefore critical that the community support advancing gas-grain chemical modeling efforts in the coming decade, especially those that focus on exploring the holistic evolution from molecular cloud through planet formation.**

These astrochemical models rely heavily upon both computation and experimental laboratory astrophysics investigations to determine reaction barriers, energetics, rates, and mechanisms. Such efforts are both time consuming and labor intensive, but are nevertheless essential to building reliable, physically meaningful models of chemical evolution through the star formation process. **The community must support computational and experimental laboratory astrophysics efforts aimed at measuring and quantifying critical pathways within astrochemical reaction networks.**

Is the fullerene and PAH content seen at the end of the stellar life cycle an unbroken link to the earlier molecular cloud, and does it form the basis of the carbon chemistry for the next generation of stars and planets?

This is perhaps the most challenging of questions, as it brings the investigation full circle and relies upon all of the previous investigations. Answering this question will require a dedicated and collaborative effort between observational, modeling, and laboratory efforts to:

1. Quantify the pathways to PAH and fullerene formation from C_6H_6 .
2. Study the potential for the destruction of PAHs and fullerenes to form the building blocks needed to seed C_6H_6 formation in the next generation of molecular clouds.
3. Effectively model these reactions, such that testable predictions can be made using observational proxies for species such as C_6H_6 that are challenging to detect.
4. Test predictions using observations across the evolutionary spectrum, using current and planned ground- and space-based facilities across the electromagnetic spectrum.

We strongly recommend that the community support dedicated, large-scale collaborative efforts that bring together observers, modelers, and experimentalists aimed at tackling these fundamental questions about the evolution of carbon in our Universe.

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