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Ubiquitous aromatic carbon chemistry at the earliest stages of star formation

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Benzonitrile (c-C_6H_5CN, where 'c' indicates a cyclic structure), a polar proxy for benzene (c-C_6H_6), has the potential to serve as a highly convenient radio probe for aromatic chemistry, provided that this ring can be found in other astronomical sources beyond the molecule-rich prestellar cloud TMC-1. Here we present radio astronomical evidence of benzonitrile in four other prestellar, and possibly protostellar, sources: Serpens 1A, Serpens 1B, Serpens 2 and MC27/L1521F. These detections establish that benzonitrile is not unique to TMC-1; rather, aromatic chemistry appears to be widespread throughout the earliest stages of star formation, probably persisting at least until the initial formation of a protostar. The abundance of benzonitrile far exceeds predictions from models that well reproduce the abundances of carbon chains such as HC_7N, a cyanopolyyne with the same heavy atoms, indicating that the chemistry responsible for planar carbon structures (as opposed to linear ones) in primordial sources is favourable but not well understood. The abundance of benzonitrile relative to carbon chain molecules displays sizable variations between sources within the Taurus and Serpens clouds, implying the importance of physical conditions and initial elemental reservoirs of the clouds themselves.

Aromaticity has long been believed to be an integral aspect of astrochemistry. The unidentified infrared bands, a set of emission features observed at mid-infrared wavelengths (roughly from 3 to 13 μm), are thought to originate from the vibrational relaxation of polycyclic aromatic hydrocarbons (PAHs)[1–3] following electronic excitation. These bands have been observed in an astonishing range of astrophysical environments, from the expanding atmospheres of asymptotic giant branch stars or supernovae[4] to the latest stages of star formation[5], to the gas in external galaxies[6]. On the basis of these observations, it has been estimated that as much as 10–25% of interstellar carbon may be locked up in aromatic molecules[3], making these species important in the chemistry of nearly all regions. In addition, the nucleation and accretion of the largest of these molecules may be a key driver for the growth of carbonaceous interstellar dust grains in the atmosphere of certain evolved stars. Among the more than 200 molecules definitively detected in the interstellar medium so far[7], however, only a very small fraction are aromatic either in a strictly chemical sense or otherwise: cyclopropenylidene (c-C_3H_2, where 'c' indicates a cyclic structure), benzene (C_6H_6), three fullerenes (C_{60}, C_{60}^+ and C_{70})[8–14] and the simplest aromatic nitrile, benzonitrile (C_6H_5CN), which was recently identified in the molecule-rich, prestellar Taurus Molecular Cloud (TMC-1) by radio astronomy[15]. Despite these discoveries, very little is known about how these specific aromatic molecules fit within the broader context of interstellar chemistry.

Extensive laboratory and theoretical work has established that the formation of benzonitrile from benzene and a source of chemically active nitrogen, commonly the CN radical, is efficient under interstellar conditions[15–19]. The presence of benzonitrile is thus a direct and meaningful indicator of radio-invisible benzene. Although the column densities of many carbon chains in cold cores such as TMC-1 are well reproduced by astrochemical models based on reactions starting with small hydrocarbon precursors[20–23], that of benzonitrile is in excess of predictions from the same model, suggesting other routes to form aromatic species may be operative in this source[15].

In this context, two consequential lines of inquiry in dark cloud chemistry follow: the extent to which the unusually rich chemistry in TMC-1 is broadly representative of dark clouds, and how differences in cloud properties affect this chemistry. TMC-1 is known to harbour unsaturated carbon chains in remarkably high abundance even relative to other dark clouds[24,25]. Many such chains were first or only detected in the interstellar medium toward this source (see ref. [7] and references therein). However, whether the chemical inventories of dark clouds commonly extend to aromatic molecules has been a topic largely confined to conjecture until very recently. The newfound ability to infer the population of benzene by radio astronomy now affords one the opportunity to assess cloud chemistry from a distinctly different viewpoint. This fundamental organic ring, owing to its much higher degree of saturation, may be formed by pathways unlike those invoked for highly unsaturated carbon chains, and is thought to be the key building block in the synthesis of far more complex organic molecules[26–28]. To substantively advance this discussion, however, it is first necessary to establish whether benzonitrile (and thus benzene, by inference) is present beyond TMC-1 and, if so, to what degree this ring is widespread in molecular clouds.

Long-carbon-chain molecules, such as the well-known cyanopolyynes (HC_nN, where n is odd), are readily observed throughout the various stages of star formation, and are particularly common at the earliest stages, before the desorption of saturated molecules from ice, which occurs when the protostellar object warms up the surrounding material[29]. And, in particular, high column densities of large cyanopolyynes, such as HC_7N and HC_9N, can provide

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evidence for sources rich in complex hydrocarbons. Given that HC_7N, a highly unsaturated (H≪C) chain, has the same heavy atoms as benzonitrile, we searched for radio lines of benzonitrile towards sources with high column densities of this species as an indicator of a rich gas-phase carbon chemistry with many of the essential building blocks to produce benzene. We discuss four sources with $N_{HC_7N} > 10^{12}$ cm^{-2} (refs. [30,31]) that were first targeted: Serpens 1a (S1a), Serpens 1b (S1b), Serpens 2 (S2) and MC27/L1521F, along with TMC-1, where benzonitrile was originally discovered.

The five sources reside in two distinct parent clouds and probe different stages of prestellar environments. The Serpens sources are all part of the same greater filament studied by Friesen et al.[31]. Based on its molecular line widths, lack of embedded protostars and small continuum-derived mass, S2 is thought to be a very young starless core, with a maximum estimated age of 10^5 years (ref. [31]). S1a and S1b are two cores straddling a central protocluster where infall is occurring and have estimated ages of several 10^5 years (ref. [31]). Both TMC-1 and MC27/L1521F are associated with the larger Taurus Molecular Cloud Structure. TMC-1 is a well-studied prestellar molecular cloud with minimal infall motion, whose age has been estimated to be ~$2–5\times10^5$ years (refs. [15,32–35]). MC27/L1521F is considered a very-low-luminosity object, where the embedded protostar is just beginning to heat up[36].

Our observations were performed with the 100 m Robert C. Byrd Green Bank Telescope (GBT) as part of a large ongoing observing campaign: A Rigorous K/Ka-Band Hunt for Aromatic Molecules (ARKHAM), which is slated to survey more than dozen sources when it is complete. An updated analysis of C_6H_5CN in TMC-1 (ref. [35]) has also been possible with additional observations from our companion survey, GOTHAM (GBT Observations of TMC-1: Hunting for Aromatic Molecules; ref. [37]). For each source, four strong benzonitrile transitions were targeted between 22 and 26.5 GHz with the K-band Focal Plane Array[38] and VEGAS spectrometer[39] (Supplementary Tables 1 and 2). For S2 and MC27/L1521F, additional observations were performed with the Ka-band receiver and target four other transitions between 28 and 30.5 GHz. MC27/L1521F also has several lower frequencies across the K band between 22 and 26 GHz. The GOTHAM observations towards TMC-1 cover transitions in the X, K and Ka bands, and are discussed in detail elsewhere[15,37].

Three transitions of benzonitrile were ultimately detected in each of our new four target sources (Supplementary Figs. 2, 4, 6 and 8). The same analysis procedure for the GOTHAM data[35] was employed here, in which a Markov chain Monte Carlo (MCMC) fit is used to determine the total column density across all energy states (N_T), excitation temperature (T_{ex}), linewidth (ΔV) and source velocity (v_{lsr}) or velocities that best reproduce the observations; details of this procedure are given in the 'Spectral stacking routine' section of the Methods, with a complete description provided in ref. [35]. Transition frequencies, line strengths and the partition function for C_6H_5CN were taken from previous laboratory measurements[15,40]. The velocity-stacked spectra from transitions towards each of the five sources (Fig. 1) show that benzonitrile is detected at least 5σ in both the velocity-stacked spectra and peak impulse response of the stack. The relative ease with which this polar ring has been observed in all five sources suggests that aromatics can survive through the formation of a protostar and perhaps beyond.

Although spectra from all five sources were fitted with one or more velocity components, the present single-dish data provide little meaningful spatial information. As such, we first examined the total abundance of C_6H_5CN in each source across all velocity components. For all but TMC-1, the primary uncertainty in the derived column densities arises from the degeneracy between this quantity and the excitation temperature, which can be mitigated by observing transitions over a still wider range of upper state energies. Towards TMC-1, the largest uncertainty is due to the unconstrained source sizes of the velocity components. Ultimately, high-sensitivity mapping with the Very Large Array in a compact configuration or ARGUS mapping with GBT is needed to better constrain the spatial extent of the emission features. Nevertheless, as indicated in Fig. 2, the C_6H_5CN abundance relative to H_2 ranges between approximately 10^{-11} and 10^{-10}, with the highest values towards TMC-1. The Supplementary Information provides considerable additional information on the uncertainties, source sizes, derived column densities and so on for each source studied here.

Overlaid on Fig. 2 are abundance predictions of C_6H_5CN and C_6H_6 from a gas–grain kinetic chemical model, NAUTILUS[41], which has been extended beyond that reported in ref. [15] and ref. [23] to account for new molecular identifications in the GOTHAM and ARKHAM surveys (see the 'Astrochemical modelling' section of the Methods, refs. [35,37,42,43] and B.A.M. et al. (manuscript in preparation)). It is clear from Fig. 2 that the derived abundances of benzonitrile are consistently at least an order of magnitude higher than those predicted from our most up-to-date models, implying that aromaticity is more important in prestellar chemistry than previously thought. In contrast, the same model well reproduces the abundance of HC_7N and even HC_9N (ref. [35]). Taken together, we conclude that the formation of aromatic molecules is quite favourable, but notably less constrained than that of highly unsaturated carbon chains.

With respect to TMC-1 specifically, we note the observationally derived and model-predicted abundances of benzonitrile differ from those reported earlier[15]. In terms of the derived abundance, the more accurate methods adopted here and in the GOTHAM survey[35] result in a value that is four times higher. Regarding the chemical models, the predicted abundances are lower by about an order of magnitude primarily for two reasons. First, the use of slightly different initial elemental abundances in our latest model[35] produces cyanopolyynes in higher abundance, but is less efficient for cyclic species. And second, the addition of new reactions (Supplementary Information, see also ref. [42] and B.A.M. et al. (manuscript in preparation)) in our network to produce other newly discovered aromatic molecules reduces the abundance of benzene and, by extension, benzonitrile.

The underproduction of cyclic molecules in our models is not limited to benzonitrile but extends to three other ring species detected with GOTHAM: 1- and 2-cyanonaphthalene (B.A.M. et al., manuscript in preparation), a pair of CN-functionalized PAHs ($C_{10}H_7CN$), and cyano-cyclopentadiene[42], a highly polar five-membered ring (c-C_5H_5CN). For both rings, deviations between derived and predicted abundances are even more disparate than for benzonitrile. Nevertheless, this same model well reproduces the abundance of two newly discovered nitrile-terminated chains, propargyl cyanide ($HCCCH_2CN$)[37] and $HC_{11}N$ (ref. [35]), which are described in accompanying GOTHAM papers. This finding again suggests that our present understanding of interstellar aromatic chemistry is demonstratively incomplete.

To determine the extent of aromatic chemistry outside of the carbon-chain-rich source of TMC-1, we compared the relative abundance ratios between HC_7N, HC_9N and C_6H_5CN in each source (Fig. 3). For S1b and S2, the column densities of HC_7N were adopted from ref. [31], whose observations were also done with the K-band Focal Plane Array on the GBT. Although the inverse relation of cyanopolyyne abundances with chain length[21,44] is fairly consistent between all five sources, the abundance ratios involving C_6H_5CN vary considerably between the Taurus and Serpens sources. In each of the three Serpens sources, the HC_7N/HC_9N ratio is comparable to the chain/ring ratio using the HC_7N/C_6H_5CN and HC_9N/C_6H_5CN ratios as metrics. In contrast, in TMC-1 and to a lesser extent MC27, the HC_7N/C_6H_5CN ratio is considerably higher, indicating that aromatic chemistry is less prevalent relative to carbon chain chemistry among sources in Taurus. We note that the derived excitation

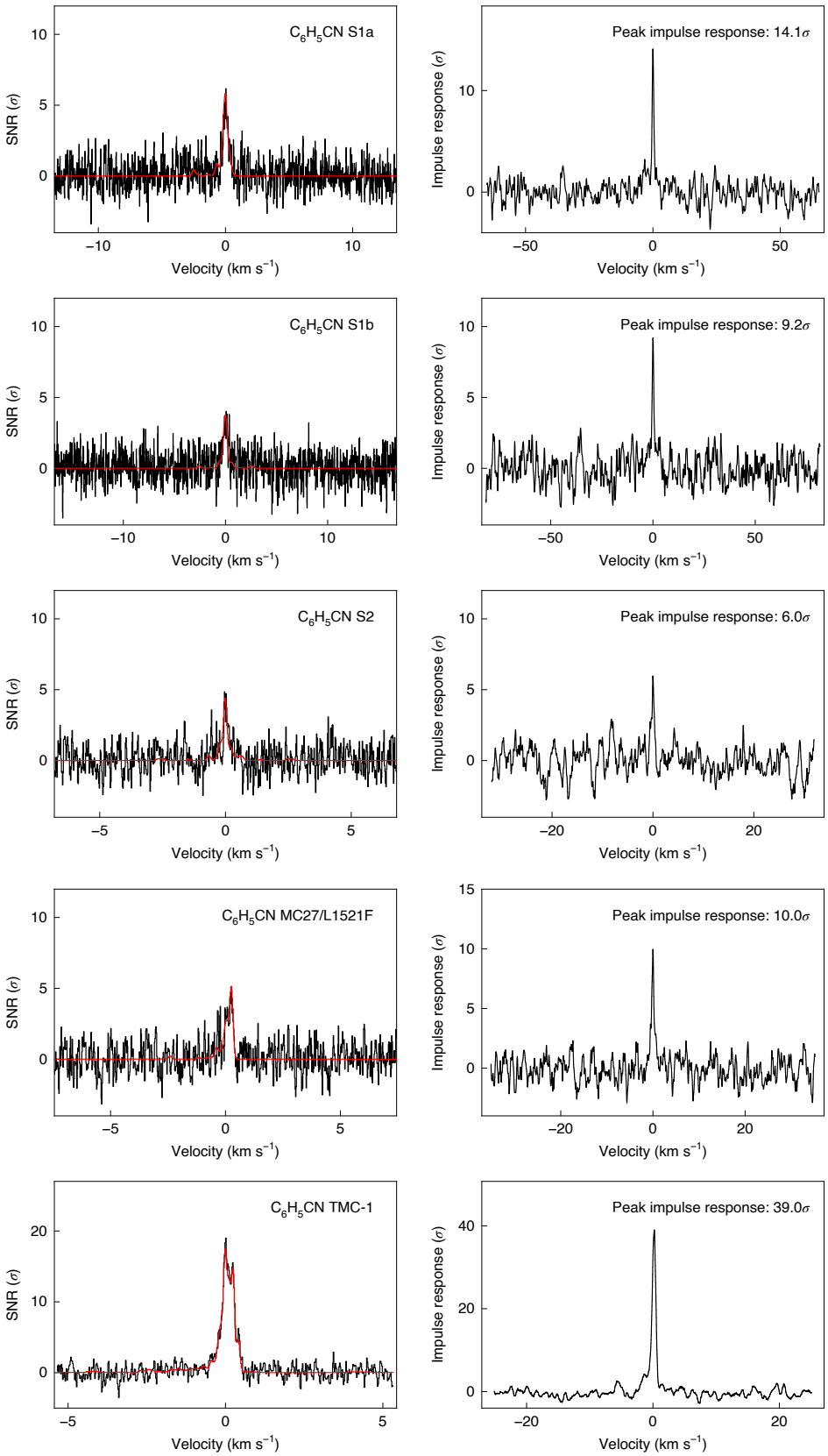

Fig. 1 | Velocity-stacked spectra of C_6H_5CN and the impulse response function of the stacked spectra in the five sources observed here. Left: velocity-stacked spectra are in black, with the corresponding stack of the simulation using the best-fit parameters to the individual lines in red. The data have been uniformly sampled to a resolution of 0.02 km s^{-1}. The intensity scale is the signal-to-noise ratio (SNR) of the spectrum at any given velocity. Right: the impulse response function of the stacked spectrum generated using the simulated line profile as a matched filter. The intensity scale is the SNR of the response function when centred at a given velocity. The peak of the impulse response function provides a minimum significance for the detection noted in each plot. See ref. [35] for details.

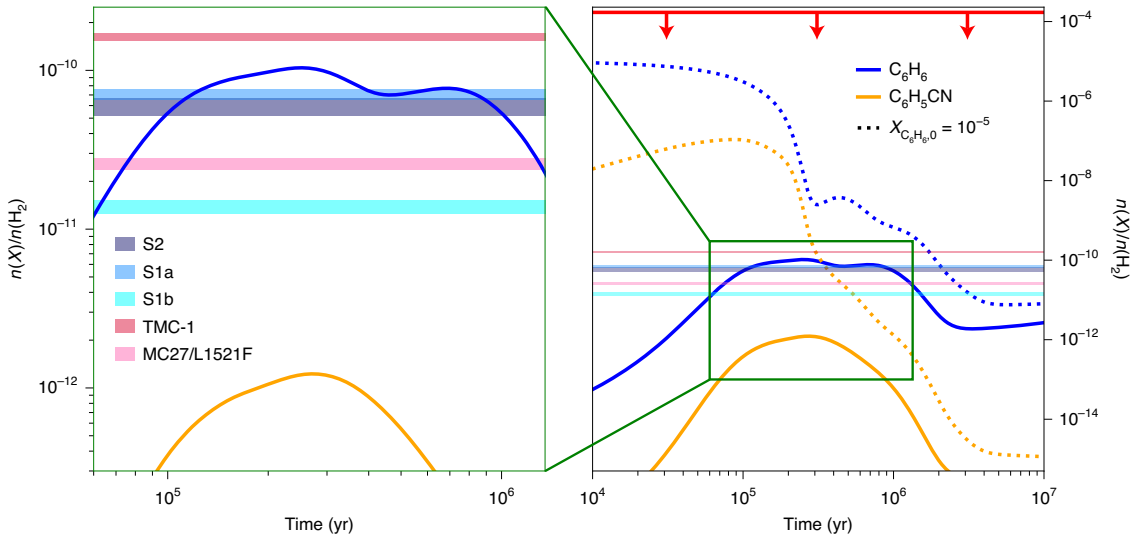

Fig. 2 | Simulated abundances with respect to hydrogen from NAUTILUS chemical models for C_6H_6 and C_6H_5CN in comparison to that derived for C_6H_5CN from observations in the five sources studied here. Uncertainties (as described in Supplementary Tables 4–8) are shown by the depth of the bars for each source in the same colours as Fig. 3. Left: zoom-in at the time frame relevant for ARKHAM sources, highlighting that the observed abundances are far greater than predicted by existing models (solid orange and blue lines). Right: Modelled and observed abundances, in addition to a simulation with an initial C_6H_6 abundance of 10^{-5} (dotted lines). The initial elemental carbon abundance, or the model's total reactive carbon budget, is shown in red with downward arrows.

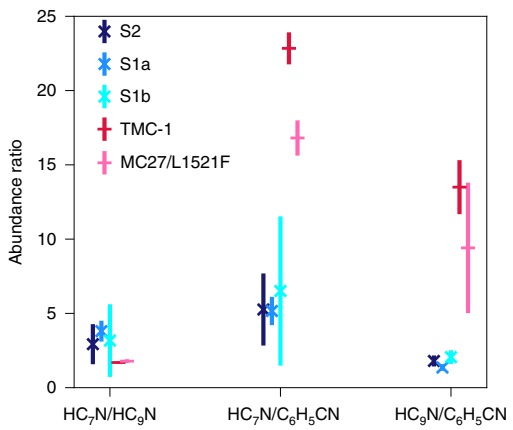

Fig. 3 | Derived abundance ratios between HC_7N, HC_9N and C_6H_5CN for each of the five sources studied here. The colours and markers are based on the parent cloud in which they reside: blue crosses for Serpens and red dashes for Taurus. The HC_7N abundances for S2 and S1b are from a previous GBT Survey by Friesen et al.[31]. Uncertainties are described in Supplementary Tables 4–8 (the last of which is adapted from table 2 in ref. [37]).

temperatures are also similar among sources from the same parent cloud, $T_{ex} \approx 11.1$–11.5 K for the Serpens sources and 4.9–6.1 K for the two sources in Taurus (MC27/L1521F and TMC-1), notwithstanding the small sample size and aforementioned degeneracy between the excitation temperatures and the derived column densities.

Similarities among related sources may indicate the importance of the parent cloud in determining the abundances of interstellar molecules, including aromatics. For example, if aromatic molecules are simply relics that have survived the diffuse cloud stage, their abundances should be largely uncorrelated with those of cyanopolyynes that are readily formed in dark clouds. If correct, large variations in the HC_7N/C_6H_5CN ratio might be expected. Alternatively, although no correlation was found between evolutionary stage and the benzonitrile abundance, if aromatics are produced in dark clouds but with different efficiencies compared with carbon chains, the HC_9N/C_6H_5CN ratio may be considerably more sensitive to the physical conditions and initial elemental reservoirs of the clouds themselves, particularly the C/O ratio, as seen in Fig. 4. Regardless, the presence of C_6H_5CN towards the very-low-luminosity object MC27/L1521F, which displays evidence for an incipient protostar, at any significant level implies that aromatic species survive at least the initial phase of star formation.

It should be emphasized that there is considerable evidence casting doubt on the importance of inheritance by simple aromatics, but the same may not be true for larger species. Several studies conclude that small PAHs (<20–30 atoms) are readily dissociated by starlight in high yield when transiting the diffuse gas[45–47] because they are unable to efficiently radiatively relax following absorption of an ultraviolet photon. If C_6H_6 is present at the beginning of the dark cloud phase, for example, our models (Fig. 2) require an abundance of ~10^{-5}, or nearly 60% of the model's reactive carbon budget (accounting for the six carbons in benzene), to reproduce the benzonitrile abundance on the timescale of prestellar sources. A similar large initial seed of cyclic species is also required to reproduce the abundance of the cyanonaphthalenes (B.A.M. et al., manuscript in preparation) and cyano-cyclopentadiene[42]. Placing such a large fraction of all carbon in a single molecule seems highly unrealistic given that the estimated fraction of carbon locked up in PAHs overall is estimated to be 10–25% (ref. [3]), and because one might expect the initial aromatic reservoir to be dominated by larger, more stable cyclic species. However, the dissociation of large cyclic species in the diffuse clouds may produce modest-sized molecular fragments that could conceivably be important precursors for small aromatic species, but are not considered here. Previous studies suggest that PAHs undergoing Coulomb explosion primarily produce hydrogen, acetylene (C_2H_2) and carbon chains containing 10–15 ($\pm$3) carbon atoms, depending the internal energy and the size of the PAH[45,47]. More generally, our modelling highlights the existence of a previously unknown and non-negligible reservoir of

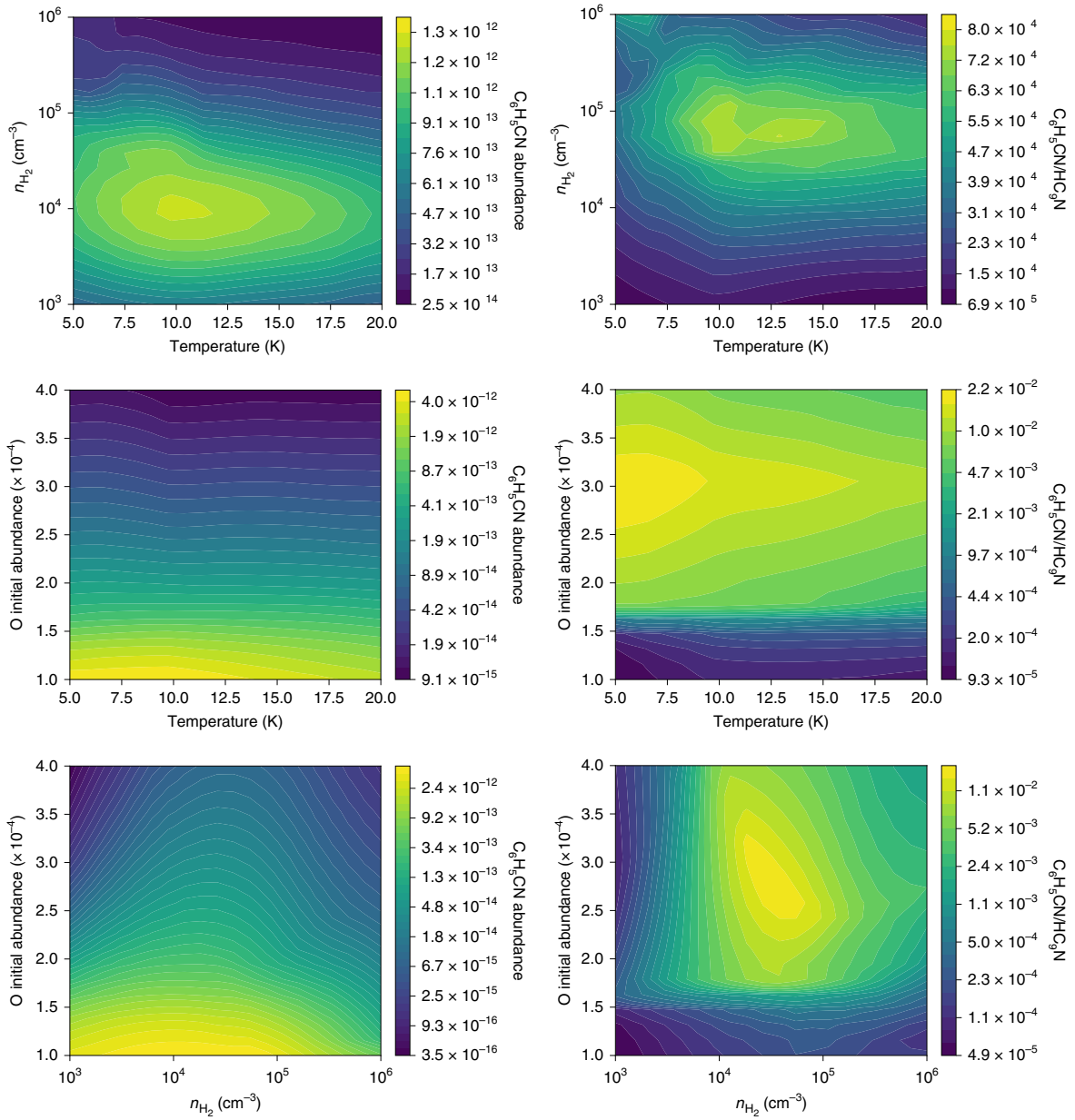

Fig. 4 | Simulated abundances and abundance ratios from NAUTILUS chemical models over a range of gas and grain temperatures, gas densities and initial elemental oxygen abundances. Left: C_6H_5CN abundances. Right: C_6H_5CN/HC_9N abundance ratios.

complex carbon that should be considered in chemical models of protostellar evolution.

In summary, the detection of benzonitrile towards the starless cloud core TMC-1 expanded our view of aromatic chemistry beyond the initial factories of carbon-rich stars. The ease with which the same aromatic species has been subsequently detected in other molecular clouds points to the generality of this chemistry in early star formation, rather than an anomaly specific to the rich carbon chain chemistry of TMC-1. The high abundances of this aromatic molecule are far greater than those predicted by present chemical models, and exhibit sizable variations between clouds of roughly similar ages. For these reasons, the present observations should serve as a strong impetus for new laboratory and theoretical studies to investigate the formation pathways of small aromatics in greater detail, and motivate additional observations towards objects over a variety of initial conditions or further along the pathway to star formation.

Methods

Spectral stacking routine. Full details of the methodology used to detect and quantify molecules in our spectra are provided in ref. [35]. Briefly, we first perform a standard steepest descent fit to the molecules in our data using model spectra generated with the formalisms outlined in Turner[48], which include corrections for optical depth, and adjust for the effects of beam dilution. The specific transition parameters for each species are obtained from spectral line catalogues primarily pulled from publicly accessible databases (https://spec.jpl.nasa.gov and https://cdms.astro.uni-koeln.de/) or generated from spectroscopic parameters provided in their respective publications. Full details for each catalogue are provided in the Harvard Dataverse repositories described below. The substantial number of transitions used in the analysis makes in impractical to provide a table of parameters in the text. Instead, the interested reader is referred to the catalogue files in the online supplementary data, which contain all of the required information in a machine-readable format. For each source, we fit either one or two distinct velocity components (v_{lsr}), and simultaneously fit for column densities (N_T), source sizes (θ_s), excitation temperatures (T_{ex}) and linewidth (ΔV).

In the case of benzonitrile, there are many transitions covered by our spectra that are not visible above the local root mean squared noise level of the

observations. We therefore extract a small portion of the observations centred around each spectral line. An SNR weighted average of these spectra is then performed based on the expected intensity of the line (derived from the MCMC parameters) and the local root mean squared noise of the observations. For the purposes of this analysis, largely due to hyperfine splitting, we treat the signals on a per-line basis rather than a per-transition basis. The result is that the stacked feature is broadened, as the hyperfine components and velocity components are not collapsed, but there is no overcounting of flux. This results in a substantial increase to the overall SNR, with the spectrum now encapsulating the total information content of all observed lines, rather than only that from the brightest lines. Finally, the model spectra are stacked using identical weights, and that stacked model is used as a matched filter that is cross-correlated with the stacked observations. The resulting impulse response spectrum provides a lower-limit statistical significance to the detection. As the filter contains the same broadened hyperfine and velocity structure as the stack, there is no loss in significance.

Supplementary Table 2 shows the total number of transitions (including hyperfine components) of the molecules analysed in this paper that were covered by GOTHAM and ARKHAM observations at the time of analysis and were above our predicted flux threshold of 5%, as discussed in ref. [35]. Also included are the number of transitions, if any, that were coincident with interfering transitions of other species, and the total number of lines used after excluding interlopers. Observational data windowed around these transitions, spectroscopic properties of each transition and the partition functions used in the MCMC analysis are provided in Harvard Dataverse repositories[49,50].

Astrochemical modelling. A modified gas–grain kinetic chemical model, NAUTILUS[41], with adaptations beyond ref. [15] and ref. [23], was used to model the formation of aromatic species. We note that the model described here uses an identical chemical network and initial parameter set (Supplementary Tables 9 and 10) to the GOTHAM-related works in refs. [35,37,42,43] and B.A.M. et al. (manuscript in preparation) unless specifically stated otherwise.

For this work, we have added the reactions summarized in Supplementary Tables 11 and 12, which expand on those presented in ref. [15]. In our models, the dominant formation pathway to benzene is through the following dissociative recombination process proposed by McEwan et al.[51]:

$$C_6H_7^+ + e^- \longrightarrow H + C_6H_6 \quad (1)$$

The fact that our model underproduces benzonitrile is indicative of some deficiency in the included aromatic chemistry, such as missing formation routes or incorrect reaction rates. For example, the cyclization of linear-carbon-chain species, either in the gas or on grains, represents an attractive possible formation pathway that is not included in our network. Moreover, only ~1% of C_6H_5CN is frozen on grains in our model; however, this value could plausibly be much greater in astrophysical environments, especially if there exists a viable grain-surface formation pathway. If so, additional low-temperature desorption mechanisms, such as sputtering by cosmic ray bombardment or accelerated gas-phase particles[23,52] will need to be considered in dark cloud chemistry models. Another possibility is that some of the as-yet-undetected species that have been proposed[53] to be important precursors to benzene—such as $C_6H_7^+$, 1,3-butadiene and propene—may be likewise underpredicted in our model, thereby resulting in low calculated abundances of C_6H_6. Interstellar observations of these potential precursors would substantially help to constrain the proposed pathways leading to benzene.

Destruction routes that lead to other aromatic or cyclic molecules, such as cyanonaphthalene and cyano-cyclopentadiene, have also been included in our latest model. However, expanding the network to include additional reactions with potential precursors to benzene, such as $C_6H_7^+$, 1,3-butadiene ($CH_2CHCHCH_2$) and the propargyl (CH_3CHCH_2) and phenyl (C_6H_5) radicals[53], did little to increase the abundance of benzonitrile.

Although our models do not reproduce the derived abundances of benzonitrile, we have explored their sensitivity to certain key parameters in our simulations to study the importance of the parent cloud to the production of benzonitrile and, by proxy, other aromatics. In Fig. 4, the calculated abundances of C_6H_5CN and the abundance ratios of C_6H_5CN/HC_9N are shown over a range of temperatures, densities and initial oxygen abundances. From the top-left panel of Fig. 4, it can be seen that there is an optimal temperature (10 K) and density (~10^4 cm^{-3}) that maximize the C_6H_5CN abundance, which is in agreement with our model's initial parameters (Supplementary Table 9). Thus, the observed aromatic chemistry is much richer than that predicted by our models over a wide range of physical conditions (left column of Fig. 4). As expected, the formation of both long carbon chains and cyclic species is strongly correlated with the C/O ratio, as an increase in available C enhances the abundance of many carbon-bearing species. When the initial oxygen abundance with respect to hydrogen is ~$2–3.5\times10^{-4}$, resulting in a carbon-poor ratio (C/O ≈ 0.5–0.85), the production of C_6H_5CN relative to HC_9N becomes more efficient. This is perhaps because the C/O ratio becomes increasingly more important as one considers the formation of longer carbon chains. Meanwhile, the dominant benzene pathway in this model does not require the presence of chains larger than five carbons. Similar to the C/O ratio, relative C_6H_5CN production seems to be favoured over HC_9N in denser (~5×10^5 cm^{-3}) gas, probably due to higher collision rates increasing the efficiency of the ion-neutral reactions in the benzene pathway and the destruction of the longest, and thus least stable, carbon chains. These scenarios underscore that it is feasible to produce significant variations between the abundance of cyanopolyynes and cyclic species simply by changing the initial conditions, which could explain the different HC_9N/C_6H_5CN ratios seen towards Taurus and Serpens.

Data availability

The datasets analysed during the current study are available in the Green Bank Telescope archive (https://archive.nrao.edu/archive/advquery.jsp). A user manual for their reduction and analysis is also available (https://go.nature.com/3npRxW5). For the ARKHAM survey, the complete, reduced survey data are available in the Harvard Dataverse Archive[50]. For the GOTHAM survey, the complete, reduced survey data in the X band are available as supplementary information in ref. [37]. The individual portions of the reduced spectra used in the analysis of the individual species presented here are available in the Harvard Dataverse Archive[49].

Code availability

All codes used in the MCMC fitting and stacking analysis presented in this paper are open source and publicly available at https://github.com/ryanaloomis/TMC1_mcmc_fitting.

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Author contributions

All authors contributed to the design of the GOTHAM and ARKHAM survey and helped to revise the manuscript. A.M.B and B.A.M. performed the astronomical observations and subsequent analysis. R.A.L., K.L.K.L. and B.A.M. performed the spectral fitting analyses. A.M.B. and C.N.S. contributed to or undertook the astronomical modelling and simulations. A.M.B., M.C.M. and B.A.M. wrote the manuscript with the help of C.N.S.

Competing interests

The authors declare no competing interests.

Additional information

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