ASTROCHEMISTRY

Detection of the aromatic molecule benzonitrile (*c*-C$_6$H$_5$CN) in the interstellar medium

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Polycyclic aromatic hydrocarbons and polycyclic aromatic nitrogen heterocycles are thought to be widespread throughout the universe, because these classes of molecules are probably responsible for the unidentified infrared bands, a set of emission features seen in numerous Galactic and extragalactic sources. Despite their expected ubiquity, astronomical identification of specific aromatic molecules has proven elusive. We present the discovery of benzonitrile (*c*-C$_6$H$_5$CN), one of the simplest nitrogen-bearing aromatic molecules, in the interstellar medium. We observed hyperfine-resolved transitions of benzonitrile in emission from the molecular cloud TMC-1. Simple aromatic molecules such as benzonitrile may be precursors for polycyclic aromatic hydrocarbon formation, providing a chemical link to the carriers of the unidentified infrared bands.

The mid-infrared spectra, roughly from 3 to 20 μm, of the interstellar medium (ISM) and photodissociation regions in both our Galaxy (*1*) and external galaxies (*2*) are dominated by emission features commonly referred to as the unidentified infrared (UIR) bands. Because prominent UIR features closely agree with the characteristic vibrational frequencies of aromatic C-C and C-H bonds, it is now widely accepted that polycyclic aromatic hydrocarbons (PAHs), along with fullerenes such as the recently detected C$_{60}^+$ molecule (*3*) and their closely related derivatives, are probably the carriers responsible for most of these features (*4*). A substantial fraction of interstellar carbon is calculated to be in the form of PAHs [~10% (*5*)], yet the origin of these aromatic species is a topic of considerable debate. In the diffuse ISM and PDR regions, where 30 to 60% of the carbon is locked up in dust grains (*6*), top-down models of PAH formation—through the destruction of dust grains by the harsh radiation environment, shock waves, or both—may be viable pathways (*7*). In denser molecular clouds, which are not subject to the ultraviolet radiation and have not been subject to shocks, other pathways must exist to synthesize these species from smaller precursor molecules.

Despite the widespread acceptance of PAHs as a common class of interstellar molecules, no specific PAH has been identified in the ISM, either by rotational spectroscopy or by observations of its infrared features, despite sustained efforts (*8*). In the microwave and (sub-)millimeter regimes, some laboratory data do exist (*9*), but such studies are relatively uncommon. Many PAHs are poor candidates for detection through radio astronomy, both because of unfavorably large rotational partition functions and because they are either apolar or weakly polar, and thus lack sufficiently intense rotational lines (relative to linear molecules of similar composition and size). A notable exception is corrannulene (C$_{20}$H$_{10}$), a bowl-shaped molecule with a relatively large permanent dipole moment [2.07 debye (*10*)], but astronomical searches for that molecule have been unsuccessful as well (*11*). In the infrared, although a concerted effort has been undertaken to catalog both laboratory and theoretical vibrational and Raman spectra of PAHs (*12*), the structural similarities among individual species result in spectra that are often indistinguishable at the modest resolving power that can routinely be achieved by astronomical observations; as a result, aggregate spectra consisting of many PAHs are invoked to reproduce astronomical features (*4*).

For these reasons, many attempts to understand the chemistry of PAHs have focused on the possible formation pathways that proceed through more readily detectable molecules. Much effort has been centered on modeling the formation of small five- and six-membered aromatic rings and their subsequent reactions with smaller hydrocarbons and nitrogen species to produce PAHs and polycyclic aromatic nitrogen heterocycles [PANHs (*13*)]. To date, the only interstellar detection of a five- or six-membered aromatic ring is benzene (C$_6$H$_6$), through the observation of a single weak absorption feature arising from its v_4 bending mode near 14.85 μm in a handful of sources (*14–17*). The lack of a permanent di-

pole moment, however, precludes the identification of benzene via its rotational transitions.

Here, we searched for a number of simple aromatic molecules, including several PA(N)Hs and nitriles (R–C≡N), a class of molecules believed to give rise to a common UIR feature at 6.2 μm (*18*). The astronomical source targeted in these observations was the cold-core Taurus Molecular Cloud 1 (TMC-1), which has long been known to possess a rich chemistry dominated by unsaturated carbon-chain molecules such as the cyanopolyynes (HC$_n$N; *n* = odd) [e.g., (*19–22*)]. The initial search was performed by construction of velocity-stacked composite-average spectra of 12 target molecules (Fig. 1) (*23*) using existing survey data taken with the Nobeyama 45-m telescope (*19*). This method enhances the signal-to-noise ratio (SNR) of a potential molecular detection by averaging the signal from multiple transitions of a molecule in velocity space. These composite averages are effective preliminary indicators of a molecule in a source such as TMC-1, where spectral features are narrow (0.3 to 0.5 km s^{-1}), the line density is relatively low (~1 line per 200 km s^{-1}), and the molecules occupy a narrow range in local standard of rest (LSR) velocity (v_{lsr} = 5.5 to 5.9 km s^{-1}) (*19*). As shown in Fig. 1, the composite spectra show highly suggestive evidence for benzonitrile in this source. Nonetheless, the observation of individual transitions is required to establish a firm detection and to enable the robust determination of the molecular abundance. The sensitivity and spectral resolution of the existing survey observations, however, were insufficient for that task.

We performed observations with the 100-m Robert C. Byrd Green Bank Telescope to confirm the detection of benzonitrile by observing nine of its individual rotational transitions, using deep integrations at high spectral resolution. Because the spectral features of other molecules in TMC-1 are so narrow, ^{14}N nuclear hyperfine structure is expected to be partially resolved in benzonitrile's lower rotational transitions. Existing spectral catalogs for benzonitrile in public databases did not contain hyperfine-splitting frequencies, and existing laboratory work at high resolution was limited to measurements below 11 GHz (*24*). For these reasons, additional transitions of benzonitrile were measured in the laboratory at high resolution between 7 and 29 GHz to ensure that the astronomical data could be interpreted (*25*).

Molecules in TMC-1 are typically well described by a single excitation temperature between 5 and 10 K (*21, 22*). Under these conditions, the strongest benzonitrile transitions fall between 20 and 40 GHz. A total of 1.875 GHz of bandwidth was covered to high sensitivity (T_A^* = 2 to 5 mK) between 18 and 23 GHz. In this range, eight of the nine strongest predicted rotational transitions were observed, each with SNR ≥ 3 (Fig. 2). For six of these, characteristic ^{14}N nuclear hyperfine splitting is partially or fully resolved for one or more components (Table 1). The emission features are best described by a v_{lsr} value of 5.83 km s^{-1}, a typical velocity for molecules in this source (*19*). All other strong transitions between 18 and 23 GHz

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fell into gaps in the spectral coverage, or in regions where insufficient noise levels were achieved. Taken together, these findings establish the presence of benzonitrile in TMC-1.

A joint analysis of all the lines yields a total column density $N_T = 4 \times 10^{11}$ cm^{-2} (25), about 5% that of HC$_7$N [1.1×10^{13} cm^{-2} (21)], an unsaturated linear cyanopolyyne with the same carbon and nitrogen composition as benzonitrile, in the same source. Because the upper state energies of the observed transitions span only a narrow energy range (3.6 to 5.7 K), the excitation temperature T_{ex} could not be constrained from the present observations. Our analysis therefore assumed $T_{ex} = 7$ K, in the middle of the range of 5 to 10 K, derived from other molecules in this source (21, 22). We also constrained the linewidth to 0.4 km s^{-1}, based on the three fully resolved hyperfine components. Although these components are some of the lowest SNR features, and our data are limited by the resolution of the observations (0.08 km s^{-1}), this linewidth is consistent with that previously derived for other molecules in this source (19). Simulated spectra under these conditions (Fig. 2) are in agreement with the observations.

The pathways leading to the formation of benzonitrile at low temperature and in low-density environments have not been studied in detail. Perhaps the only promising astrochemically relevant formation pathway discussed in the literature is the neutral-neutral reaction

$$CN + c\text{-}C_6H_6 \rightarrow c\text{-}C_6H_5CN + H \qquad (1)$$
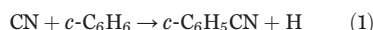
This barrierless, exothermic reaction has been considered previously (26, 27). In an effort to determine the contribution of Reaction 1 to the observed abundance of benzonitrile in TMC-1, we have modified the Kinetic Database for Astrochemistry (KIDA) gas-phase reaction network (28) to include this reaction, as well as destruction pathways from photons, ions, and depletion onto grains (25). This network was then combined with the NAUTILUS-1.1 modeling code (29) assuming elemental abundances and physical conditions appropriate for TMC-1 (30). A number of additional gas-phase formation routes for the precursor benzene were also considered and included in the modified network (25). A column density of H$_2 = 10^{22}$ cm^{-2} (22) was used to convert from modeled abundances to column densities to compare with observations. Figure 3 shows the derived column densities and those predicted by the model for benzonitrile, benzene, CN, and the cyanopolyynes HC$_3$N, HC$_5$N, HC$_7$N, and HC$_9$N. Although the calculated column densities of most of the cyanopolyynes agree with observational results within a factor of 2, the predicted benzonitrile column density is smaller than the derived value by nearly a factor of 4.

This difference may be explained by other formation routes for benzene and/or benzonitrile that are not considered in our model. For instance, experiments have found that benzene can be formed in electron-irradiated acetylene ices (31). In astrochemical models, the addition of cosmic ray–driven irradiation chemistry in the solid phase has been found to improve agreement between observational and theoretical abundances for other large interstellar molecules (32), although for such grain-surface processes to contribute to gas-phase abundances, there must exist efficient nonthermal desorption mechanisms. Recent theoretical and experimental work suggests that interactions between cosmic rays and grain surfaces could result in the liberation of solid-phase species into the gas phase via processes that are viable in cold cores such as TMC-1 (33).

Benzene is also known to be produced in irradiated acetylene gas (34). Radiation chemistry differs from photochemistry in a number of ways (35) and may be a viable formation pathway for aromatic and PAH molecules as a result of their increased photostability relative to simpler organics (36). However, there is insufficient theoretical and experimental work to include such
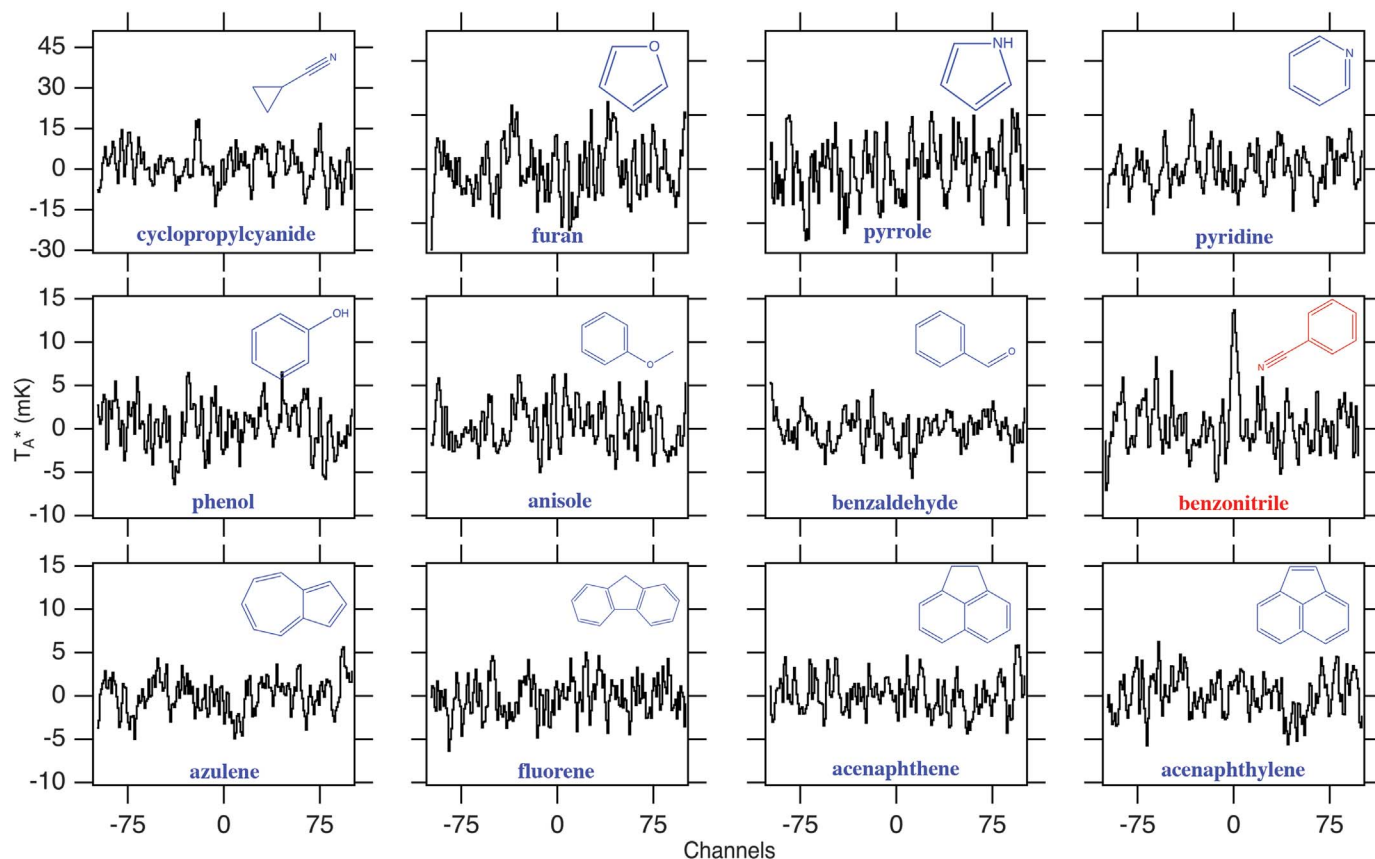

Fig. 1. Composite averages of molecules toward TMC-1. Velocity-stacked composite averages of all transitions of a given molecule with upper state energy (E_U) < 70 K constructed from the entire survey (8.8 to 50 GHz) of TMC-1 (19) are shown. The channel spacing is 20 kHz. If a molecule is present, signal in antenna temperature (T_A^*) would be expected at channel 0. A detectable signal was present only for benzonitrile (red).
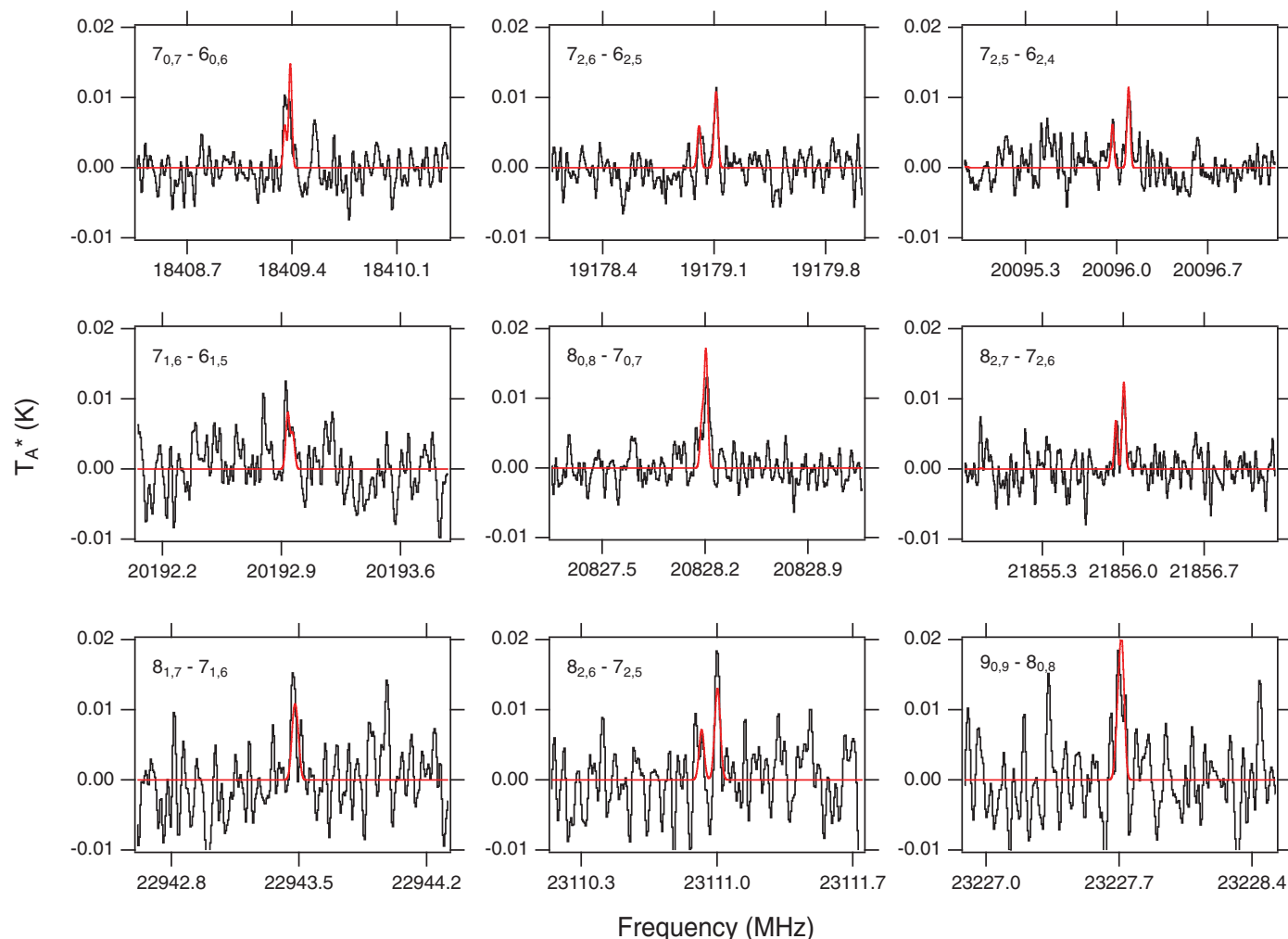
Fig. 2. Detected emission lines of benzonitrile in TMC-1. Observational spectra are shown in black smoothed to a resolution of 5.7 kHz (0.08 km s^{-1}) and shifted to a v_{lsr} value of 5.83 km s^{-1}. A simulated spectrum of benzonitrile (linewidth = 0.4 km s^{-1}, N_T = 4 × 10^{11} cm^{-2},

T_{ex} = 7 K) is overlaid in red (*25*). Rotational quantum numbers are displayed at the upper left of each panel. The four transitions with well-resolved hyperfine structure are shown on an expanded frequency axis in (*25*).

Fig. 3. Chemical model of TMC-1.
Results of a three-phase astrochemical model are shown, updated to include the benzonitrile formation pathway given in Reaction 1. The model gas-phase column densities as a function of time are given as solid colored lines. Column densities of benzonitrile, cyanopolyynes, and CN derived from observations are shown as dots with dashed horizontal lines [from top to bottom: CN, HC$_3$N, HC$_5$N, HC$_7$N, HC$_9$N, and benzonitrile (*21, 39*)]. The derived column densities are plotted at the chemical age of TMC-1 [~2 × 10^5 years (*30*)].
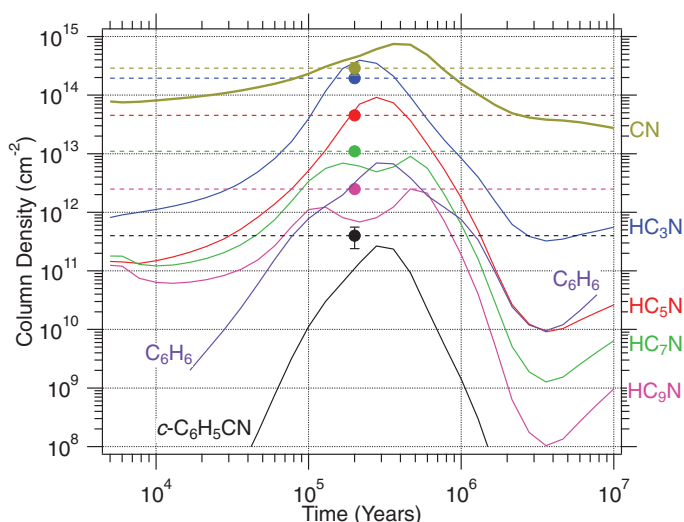
pathways in our model. Previous work also suggests a possible connection between benzonitrile and the cyanopolyynes (*21*). That work showed a sharp decrease in the calculated abundance of HC$_{11}$N relative to the abundance trend of the n(odd) = 3 to 9 cyanopolyynes, possibly due to cyclization processes for HC$_n$N molecules that could eventually lead to functionalized aromatics such as benzonitrile.

We also considered the possibility that benzonitrile itself may be a contributor to the UIR bands. The vibrational spectrum of benzonitrile has been studied in the infrared, both experimentally (*37*) and theoretically (*38*), but it does not appear in spectral databases (*12*) and is not commonly considered as a potential UIR carrier. Nonetheless, the interstellar IR emission features at 3.3 μm (C–H aromatic stretch) and 4.48 μm (C≡N stretch) are both in agreement with very strong IR modes of benzonitrile (*38*), thus making it a potential carrier in its own right, as well as a likely precursor to polyaromatic species.

Table 1. Detected benzonitrile transitions. Shown are quantum numbers, frequencies, upper state energies (E_U), line strengths ($S_{ij}\mu^2$), observed intensities (ΔT_A^*), and signal-to-noise ratio (SNR) of detected benzonitrile transitions. ΔT_A^* values reflect uncertainty in the Gaussian fit; a conservative 30% uncertainty in the absolute flux calibrated value is assumed (25). Statistical uncertainties (1σ), derived from the best-fitting constants in (25), are given in parentheses in units of the last significant digit.

Transition		Frequency (MHz)	E_U (K)	$S_{ij}\mu^2$ (debye^2)	ΔT_A^* (mK)	SNR
$J'_{K_a,K_c} - J''_{K_a,K_c}$	$F' - F''$					
$7_{0,7}-6_{0,6}$	6–5	18409.3490(2)	3.61	39.5		
	8–7	18409.3840(2)	3.61	52.9	10.3(8)[b]	4.4
	7–6	18409.3879(2)	3.61	45.7		
$7_{2,6}-6_{2,5}$	7–6	19179.0017(2)	4.52	42.4	5.4(5)	2.7
	6–5	19179.1027(2)	4.52	36.6	10.6(5)[b]	5.4
	8–7	19179.1128(2)	4.52	49.1		
$7_{2,5}-6_{2,4}$	7–6	20095.9645(2)	4.62	42.5	6.6(5)	3.3
	6–5	20096.0824(2)	4.62	36.7	10.0(2)[b]	4.9
	8–7	20096.0917(2)	4.62	49.2		
$7_{1,6}-6_{1,5}$	6–5	20192.9325(2)	4.11	39.0		
	7–6	20192.9342(2)	4.11	45.1	8(1)[b]	2.1
	8–7	20192.9632(2)	4.11	52.2		
$8_{0,8}-7_{0,7}$	7–6	20828.1746(2)	3.20	46.2		
	9–8	20828.2012(2)	3.20	59.6	11.7(9)[b]	5.9
	8–7	20828.2045(2)	3.20	52.5		
$8_{2,7}-7_{2,6}$	8–7	21855.9324(3)	5.57	49.7	7.1(4)	3.1
	7–6	21855.9944(3)	5.57	43.8	10.7(5)[b]	4.7
	9–8	21856.0064(3)	5.57	56.4		
$8_{1,7}-7_{1,6}$	7–6	22943.4640(3)	5.21	45.8		
	8–7	22943.4729(3)	5.21	52.0	16.2(8)[b]	3.2
	9–8	22943.4885(3)	5.21	59.1		
$8_{2,6}-7_{2,5}$	8–7	23110.9171(3)	5.73	49.9	6.2(9)	1.2
	7–6	23110.9923(3)	5.73	43.9	19.6(9)[b]	3.8
	9–8	23111.0042(3)	5.73	56.7		
$9_{0,9}-8_{0,8}$	8–7	23227.6903(3)	5.72	52.9		
	10–9	23227.7105(3)	5.72	66.3	16(2)[b]	3.3
	9–8	23227.7127(3)	5.72	59.3		

[b]Indicates blended hyperfine components; ΔT_A^* is the peak value of the observed feature.

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Detection of the aromatic molecule benzonitrile (*c*-C$_6$H$_5$CN) in the interstellar medium

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A specific interstellar aromatic molecule

Aromatic molecules such as polycyclic aromatic hydrocarbons (PAHs) are known to exist in the interstellar medium owing to their characteristic infrared emission features. However, the infrared emission only indicates the general class of molecule, and identifying which specific molecular species are present is difficult. McGuire *et al.* used radio astronomy to detect rotational transitions of benzonitrile emitted from a well-known nearby cloud of interstellar gas (see the Perspective by Joblin and Cernicharo). This molecule may be a precursor to more complex PAHs. The identification of benzonitrile sheds light on the composition of aromatic material within the interstellar medium—material that will eventually be incorporated into new stars and planets.

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