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Gas-phase synthetic pathways to benzene and benzonitrile: a combined microwave and thermochemical investigation

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The recent astronomical detection of benzonitrile (C_6H_5CN) in the cold, starless cloud TMC-1 demonstrates that aromatic chemistry is efficient even in the primordial stages of star and planet formation. C_6H_5CN may serve as a convenient observational proxy for benzene, which is otherwise challenging to detect in space, provided the chemistry linking these two molecules is tightly constrained. Here we present a high-resolution microwave spectroscopic study in combination with an accurate thermochemical treatment of the formation chemistry of C_6H_5CN and benzene. We demonstrate that C_6H_5CN is a highly useful tracer for benzene in the presence of CN radical, either in space or in the laboratory, and by inference, that the reaction $C_2H + CH_2(CH)_2CH_2$ yields benzene, along with its high-energy polar isomer fulvene. In addition, we find that the higher energy isomer, C_6H_5NC, is formed at $<0.1\%$ abundance relative to C_6H_5CN. By exploiting −CN tagging, formation pathways to produce benzene using a variety of acyclic hydrocarbon precursors are then explored. A robust, self-consistent, and chemically accurate theoretical treatment has also been undertaken for several key reactions. The results are discussed both in the context of aromatic molecule synthesis and astrochemistry.

1 Introduction

From infrared observations of our galaxy and numerous external ones, it is widely thought that perhaps as much as 10–25% of interstellar carbon is locked up in polycyclic aromatic hydrocarbons (PAHs),[1,2] a well-known class of organic molecules consisting of multiple fused aromatic (typically benzene) rings. PAHs are common on Earth, usually as byproducts of incomplete combustion reactions of organic material such as fossil fuels and biomass.[3,4] In the interstellar medium (ISM), PAHs may play an important role in physical and chemical evolution, helping to regulate the net charge balance in molecular clouds, as surface catalysts for molecular hydrogen formation, and as seeds of carbonaceous interstellar dust.[5] These submicron-sized dust particles can transit the interstellar gas and coagulate, providing the material from which protoplanetary disks, planetesimals, and planets are formed.[6]

Despite their apparent ubiquity, no individual PAH has been definitively identified in the ISM despite sustained efforts spanning more than 30 years.[7] The presence of PAHs has instead been inferred from the close correspondence in wavelength between strong infrared emission bands and the distinctive spectral features that characterize large aromatic molecules; using databases to fit band profiles, a mixture of PAHs are thought to give rise to these astronomical features. In contrast, more than 200 individual species have been unambiguously detected in the ISM *via* their gas-phase rotational spectra using radio astronomy.[7] Very recently, benzonitrile (C_6H_5CN; hereafter BN), was identified in the ISM by rotational spectroscopy, the first benzene derivative to be identified in this way.[8] While BN is not a PAH, it is widely accepted that the bottleneck in PAH growth is the cyclization of the first aromatic ring,[9] normally either phenyl radical (C_6H_5) or benzene (C_6H_6). By this reasoning, BN has the potential to provide observational constraints at the very earliest stages of the aromatic chemistry that ultimately dominates the carbon budget of the ISM, particularly if its formation can be closely linked to that of benzene.

The difficulty associated with the astronomical detection of benzene is two fold: its infrared vibrational transitions are blocked by atmospheric absorption, and it has no permanent dipole moment (thus no allowed pure-rotational spectrum) owing to high symmetry (D_{6h}). Observations of C_6H_6 have thus far been limited to space-based infrared telescopes that are capable of detecting its vibrational transitions. As a result, C_6H_6 has only

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been reported in absorption against a handful of bright sources using the Spitzer Space Telescope and the Infrared Space Observatory.[10–12] However, if the chemistry linking BN to benzene can be well-constrained then BN becomes a meaningful proxy for this fundamental aromatic ring. This in turn would allow studies of the formation and reactions of aromatic molecules across the far wider range of physical and chemical environments, and evolutionary timescales, that are accessible with ground-based, radio astronomical observations.

Here, we systematically explore the formation chemistry of BN, and by inference that of benzene, using a combination of isotopic- and isomer-specific rotational spectroscopy and quantum chemical calculations, building on extensive prior theoretical work, and elegant mass spectrometric studies. Specifically, we: (1) experimentally investigate the benzene + CN reaction at high spectral resolution to determine the branching ratio between BN and its isomer phenyl isocyanide (C_6H_5NC; hereafter PIC) under our experimental conditions; (2) test a variety of astrophysically relevant reactants which are postulated to form benzene, and using –CN as a tag, observe the production of BN and other species *via* cm-wave rotational spectroscopy; (3) determine the abundance of benzene and its high-energy, polar isomers in the C_2H + $CH_2(CH)_2CH_2$ reaction in the absence and presence of the –CN tag, to estimate benzene production relative to that of other C_6H_6 isomers, and (4) present a self-consistent quantum mechanical treatment of the reaction network that leads to BN using composite methods which routinely reach chemical accuracy ($\lesssim 4$ kJ mol^{-1}). The astronomical consequences of these new findings are then discussed.

2 Experimental techniques

A high sensitivity cavity-enhanced, Fourier-transform (FT) microwave spectrometer,[13,14] based on the original design of Balle & Flygare,[15] was used in the present investigation. Its spectral resolution is also very high, of order 0.1 ppm, allowing rotational transitions of different isomers and isotopic species to be trivially separated by many resolution elements (*e.g.*, 100–1000 samples), and closely-spaced hyperfine structure (of order 5 kHz; *i.e.* several resolution elements) to be routinely resolved. Furthermore, at the very low rotational temperature ($T_{\rm rot} \sim$ 1–3 K) achieved in our supersonic expansion source, spectral congestion is greatly reduced, further increasing the confidence of line assignments, even if many tens of species are simultaneously produced. With the exception of molecules that possess two atoms from the first-row of the periodic table, such as the CN and C_2H radicals, rotational transitions of many species fall within the 5–42 GHz operating range of the spectrometer.

Molecules in our instrument are produced by subjecting stable precursor gases, which are heavily diluted to $\sim$1% in inert carrier gas (typically Ne), to a dc electrical discharge ($\sim$1 kV) as they pass through the throat of a supersonic expansion source. Typical backing pressures are 2.5 kTorr. Following a relatively short transit time ($\sim$0.5 ms) through the nozzle, the resulting products undergo rapid rotational cooling as they adiabatically expand into a large vacuum chamber maintained at low pressure ($<10^{-5}$ Torr). When the fast-moving jet passes through the beam waist of the Fabry–Perot cavity, a pulse (1 μs) of microwave radiation excites molecules in the plasma. If a rotational transition lies within the $\sim$1 MHz bandwidth of the cavity, the resulting free induction decay is detected with a sensitive microwave receiver, the FT of which yields the frequency-domain signal. Frequency agility is achieved by synchronously adjusting the mirror separation and applied frequency under computer control.

Previous isotopic studies using our molecule source strongly implicate the importance of neutral–neutral reactions involving one or even two radical reactants in product formation. To explain the production of selective isotopic species, fairly direct, prompt mechanisms must be operative.[16] Ion–molecule reactions can be safely neglected with heavy buffer gases (*i.e.* Ar and Ne, used here) because the fractional ionization is known to be quite low ($\sim 10^{-6}$); the exception to this rule is use of H_2 or He, which dramatically increases the degree of ionization (10^{-4}–10^{-3}).[17] Rapid stabilization of products occurs *via* collisions (including three-body) with the buffer gas in the throat of the gas expansion, even if these species are imparted with significant internal energy during formation. In the ISM, three-body collisions that could stabilize products in a concerted fashion do not occur on relevant timescales, and even the two-body collisions are infrequent (on the order of days) with respect to the timescale of radiative processes. The efficiency of radiative relaxation as a means to dissipate excess internal energy depends on a number of factors but generally improves with increasing size owing to higher density of states (see, *e.g.*, the C_6H^- anion[18]). If radiative pathways are inefficient, fragmentation or dissociation of the product may result.[19,20]

Reactions involving radicals have been shown in a variety of laboratory experiments to be efficient even under single-collision (two-body) conditions,[21,22] suggesting these pathways can contribute to or even dominate the formation of many interstellar molecules.[23] For this reason, and despite quite different stabilization mechanisms in our molecule source compared to the ISM, there is strong circumstantial evidence that the reactions discussed here are likely, but not certain, interstellar pathways; as necessary, follow-up studies under single-collision conditions may be warranted.

3 Quantum chemical methods

The reactions investigated as part of this work have been examined previously with various quantum chemical methods. Motivated by the astronomical discovery of BN, we have re-examined the sequence of reactions that are proposed to yield BN in the ISM. Our primary aim in doing so is to provide a self-consistent, highly accurate ($\lesssim 5$ kJ mol^{-1}) set of thermochemical values and rate coefficients that describe the reaction coordinate between C_6H_6 and BN. Although higher-level calculations have been performed for some aspects of the reaction – *e.g.*, the coupled-cluster treatment by Jones *et al.*[22] on C_6H_6 – the uncertainties associated with different determinations can be difficult to ascertain. We were thus motivated to utilize a well-benchmarked scheme that provides statistically reliable and accurate thermochemistry.

Appropriately, we chose the composite G3//B3LYP scheme in our electronic structure calculations because it has been shown to yield statistically robust reaction thermochemistry for a large variety of systems (*e.g.*, closed and open-shell) at relatively low computational cost.[24] Briefly, the scheme involves geometry optimizations performed using the B3LYP density functional.[25] Geometry optimization and zero-point contributions are calculated at the B3LYP/6-31G(d) level, with electron correlation treated by a series of calculations performed at the MP2, MP4, and QCISD levels using various bases.[25] Restricted and unrestricted reference wavefunctions were used for the closed-shell and open-shell species respectively. Calculations were carried out with the Gaussian '09 suite of programs.[26]

Initial searches for stationary points were performed at the (U)B3LYP/6-31G(d) level using the growing string method (GSM), an automated reaction path search method which has been shown to reliably find transition states without requiring user intervention.[27–29] The reaction path is represented as a string of nodes (corresponding to geometries) that join the initial reactant and the final products; in the current work, typically ~36 nodes were included in each string, and were iteratively added and minimized along the string in a "growth phase". When sufficient nodes have been added, a global minimization is performed with every node, and upon convergence (defined here as a gradient RMS less than 5×10^{-4}) yields a good approximation to the exact reaction path.[29] Subsequently, stationary point geometries (*i.e.* minima and maxima) along the resulting reaction paths are refined using the G3//B3LYP scheme.

4 Results

4.1 Potential energy surface

4.1.1 Formation of benzene. Because the bottleneck in PAH growth is the first aromatic ring-closure step, detailed kinetic schemes and an abundance of theoretical calculations[9] have been put forth, largely by the combustion community. These include, but are not limited to, (1) the three-body propargyl recombination reaction $C_3H_3 + C_3H_3 + M \rightarrow C_6H_6 + M$;[30] (2) ion–molecule pathways that proceed thru $C_6H_7^+$, which might be important in Titan's ionosphere[31] and proto-planetary nebula such as CRL 618 that have high levels of ionizing radiation;[32] and (3) reactions involving 4 and 2 carbon atom reactants,[33] with the latter being either acetylene (HCCH) or the ethynyl (C_2H) radical.

Since pathways (1) and (2) are not relevant to the cold astronomical sources, such as TMC-1, we have re-investigated pathway (3) theoretically, motivated by extensive theoretical and experimental work by Kaiser and co-workers[22] who conclude the reaction between *trans*-1,3-butadiene and the C_2H radical to form benzene is both viable and facile:

$$C_2H + CH_2(CH)_2CH_2 \rightarrow C_6H_6 + H. \qquad (1)$$

This reaction is predicted to be highly exothermic, initially forming an acyclic, conjugated adduct before multiple intermediate rearrangements lead to cyclization and hydrogen atom loss to produce benzene. Our GSM calculation yielded the same reaction pathway as presented by Jones *et al.*,[22] thus providing independent confirmation without bias (*i.e.* "chemical intuition") that this route is indeed the most direct means to cyclize *trans*-butadiene with C_2H. As shown in Fig. 1, the C_2H radical adds directly to elongate the carbon chain, and cyclization occurs by connecting one end of the chain with the other. Stepwise hydrogen atom transfer and loss yields C_6H_6. Comparisons of the G3//B3LYP thermochemistry with the results of Jones *et al.*[22] are in quantitative agreement (Table 1), yielding a mean difference of 4 kJ mol^{-1} between the two sets of stationary points. An additional point of comparison can be made by using accurate heats of formation from the Active Thermochemical Tables,[34] from which we calculate the net enthalpy change at 0 K for reaction (1) to be −372.3(5) kJ mol^{-1}. This value compares favorably to that determined by Jones *et al.*[22] (−369 kJ mol^{-1}) and the G3//B3LYP value (−365 kJ mol^{-1}).

Our calculations have also been extended the work by Jones *et al.* to include *gauche*-butadiene. Although the *trans* conformer is lower in energy (by ~12.1 kJ mol^{-1} (ref. 35); see Fig. 1), the *gauche* conformation affords a kinetic advantage over the ground state *trans* isomer, having one less energy barrier to surmount. The addition of C_2H to *gauche*-butadiene forms two carbon bonds simultaneously, thus omitting an additional cyclization step. While the thermal population of the *gauche* conformer is predicted to be low at low temperature, under conditions where non-equilibrium dynamics are significant (*e.g.*, in an electrical discharge, or the ISM) the role of this conformer may be non-negligible or even significant.

It should be emphasized that other product channels beyond benzene are possible in reaction (1). In the study of Jones *et al.*,[22] the measured branching fraction for benzene was estimated to be ~30%, with the remaining product channel (70%) ostensibly the 1,3-hexadien-5-yne isomer. In a closely-related study of reaction (1) by Lockyear *et al.*[36] spectroscopic evidence was only found for the fulvene isomer in a low pressure (4 Torr), room temperature slow-flow reactor using photoionization time-of-flight mass spectrometry. However, the upper limit on the production of benzene plus 1,3-hexadien-5-yne in this experiment was high (45%), in marginal agreement with that measured or predicted (40% at 0 kJ mol^{-1}) by Jones *et al.*[22]

4.1.2 Formation of C_6H_5CN from benzene and CN. The reaction of benzene with CN radicals has been studied by a number of groups.[21,37–39] The reaction bifurcates, forming either BN or PIC depending on the orientation of the CN radical attack:

$$C_6H_6 + CN \rightarrow C_6H_5CN + H, \text{ or} \qquad (2)$$

$$C_6H_6 + NC \rightarrow C_6H_5NC + H. \qquad (3)$$

The most recent energetics by Balucani *et al.*[21] (B3LYP/6-311+G**) and Woon[37] (6-31+G**) indicate a submerged barrier (~20 kJ mol^{-1}) to PIC formation relative to the C_6H_6 + CN asymptote, while the BN

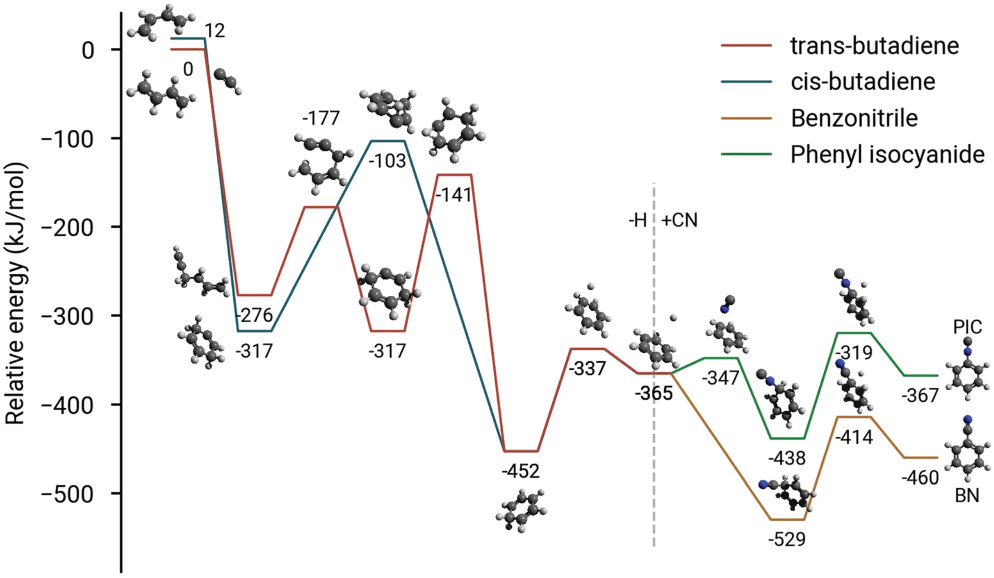

Fig. 1 Potential energy surface for the two reactions under investigation: C_2H + butadiene → benzene, as indicated to the left of the vertical dashed line (|); and benzene + CN, to the right of the dashed line. Energetics are relative to the reactant asymptote, C_2H + CN + *trans*-butadiene. The red trace shows the reaction between C_2H radicals and *trans*-butadiene, whereupon the newly formed conjugated chain undergoes cyclization and hydrogen atom transfer to yield the C_6H_7 adduct. The blue trace shows the reaction starting from *gauche*-butadiene to directly form a cyclic intermediate, which can then undergo hydrogen atom transfer to rejoin the *trans*-butadiene pathway. Subsequent hydrogen atom loss yields C_6H_6 + H. The second reaction bifurcates depending on the orientation of the CN radical. The green trace follows attack from the nitrogen end, surmounting an energetic barrier to form the $C_5H_5CH(NC)$ adduct, whereas the orange trace shows attack from the carbon end, which occurs barrierlessly to form the $C_5H_5CH(CN)$ adduct. Subsequent hydrogen atom loss yields PIC or BN respectively.

Table 1 Comparison of the G3//B3LYP and CCSD(T)/CBS[22] energetics involved between *trans*-butadiene and C_2H to form C_6H_6 + H. Ordering of the stationary points are from left to right according to Fig. 1, following the red trace. Values are given in kJ mol^{-1}, and are relative to the reactant asymptote

Stationary point	G3//B3LYP	Jones *et al.*[22]
A	−276	−282
B	−177	−181
C	−317	−318
D	−141	−144
E	−452	−457
F	−337	−345
G	−365	−368

adduct forms exothermically and barrierlessly. Subsequent hydrogen atom loss occurs exothermically for both products, although PIC formation involves a barrier in excess of the C_6H_6 + CN asymptote, while BN formation passes over of a submerged barrier of roughly the same height but one that lies well below this asymptote.

The G3//B3LYP thermochemistry reveals a qualitative difference in the benzene + CN potential energy surface relative to previous studies: formation of the PIC adduct requires surmounting a barrier of ~17 kJ mol^{-1}. Along with a second barrier that is required for H loss, these findings imply that PIC formation is highly unfavorable under low temperature conditions. A quantitative comparison of the thermochemistry performed here relative to previous studies is summarized in Table 2. Overall, the energies calculated at the G3//B3LYP level for stationary points are in agreement with previous determinations, although they align better with the B3LYP/6-311+G** calculations by Balucani *et al.*[21] The major, quantitative difference between this work and literature values lie in the barrier heights—the G3//B3LYP values are consistently higher owing to the amount of dynamic correlation retrieved in the composite method, thereby raising the barrier heights relative to the reactants. To ensure that these observations are not due to symmetry-breaking from the unrestricted Hartree–Fock reference wavefunction, we performed single-point energy calculations for the C_6H_6 + CN portion of the PES using the Bruenecker variant of the coupled-cluster method with single, double, and perturbative triple excitations [BCCSD(T)] with a modest basis set (aug-cc-pVTZ+2df). As seen in Table 2, the BCCSD(T) energetics support the

Table 2 Comparison of thermochemical thresholds for the reaction between C_6H_6 and CN radicals from this work (G3//B3LYP and BCCSD(T)//B3LYP) and previous studies. Values are given in kJ mol^{-1}, relative to the C_6H_6 + CN dissociation asymptote

Species	G3//B3LYP	BCCSD(T)//B3LYP	Balucani *et al.*[21]	Woon[37]
Phenylisocyanide				
$[C_6H_6NC]^‡$	17	10	−14	−19
$C_5H_5CH(NC)$	−74	−77	−78	−83
$[C_5H_5C(NC)\text{-}H]^‡$	45	35	30	25
PIC	−3	−3	−5	−8
Benzonitrile				
$C_5H_5CH(CN)$	−165	−165	−165	−164
$[C_5H_5C(CN)\text{-}H]^‡$	−50	−56	−62	−59
BN	−95	−93	−95	−90

Double daggers indicate transition states.

G3//B3LYP results, which suggests that the PIC pathway is endothermic relative to C_6H_6 + CN, whereas the BN formation occurs barrierlessly and is highly exothermic.

Based on comparisons with prior work, we believe the comprehensive set of energetics presented in Fig. 1 is both self-consistent and accurate. In particular, calculations pertaining to the C_6H_6 + CN reaction appear to have been significantly improved over previous values with respect to the energetics of the barrier heights. These refined values should allow subsequent kinetic analysis and chemical modeling to be performed more accurately, and are central to the interpretation of experimental findings discussed in subsequent sections.

4.2 Gas-phase synthesis of C_6H_5CN

The use of BN as a surrogate for benzene has previously been suggested by several authors,[32,40] and more recently reaction (2) was invoked by McGuire *et al.*[8] to model the astronomical abundance of BN in TMC-1. Although this reaction was previously studied under single-collision conditions and shown to be efficient,[21] the evidence for BN was indirect, having been inferred from a combination of mass spectroscopy, the experimentally determined reaction exothermicity, and the aforementioned electronic structure calculations using density functional theory. In a subsequent investigation,[38] low-temperature rate coefficients were measured for the reaction between benzene and CN radical by monitoring the depletion of CN by laser-induced fluorescence spectroscopy. In the same study, the products of this reaction were probed at room temperature using synchrotron VUV photoionization mass spectrometry. On the basis of ionization energies, evidence was only found for BN. Even though there is little ambiguity regarding the overall conclusions of prior studies, a key feature of the present method is the ability to directly detect rotational lines of BN, its isomer, PIC,[41,42] and other possible products at high sensitivity and resolution. In this way, it is possible to monitor and quantify a wide range of product outcomes, and therefore meaningfully extend previous studies, albeit under conditions that are not directly transferable to the cold, low density ISM. The branching ratio between BN and PIC is one obvious example, since only an upper limit of $\lesssim$10% PIC was inferred by Trevitt *et al.*[38]

To experimentally investigate the branching ratio between reaction (2) and (3), a discharge was applied to a dilute gas mixture of C_6H_6 and CH_3CN in Ne, and the products observed by cavity FT microwave spectroscopy. CH_3CN was chosen because it is a well known[43] source for CN radicals in an electrical discharge *via* the reaction

$$CH_3CN \xrightarrow{dc} CH_3 + CN. \quad (4)$$

Under these experimental conditions, very strong lines of BN were observed, while those of PIC are only present at trace levels. In addition to CH_3CN, the CN radical can also be produced in high yield by discharging cyanoacetylene (HC_3N):

$$HC_3N \xrightarrow{dc} C_2H + CN. \quad (5)$$

Use of this precursor gave nearly identical results: very strong lines of BN and very weak ones of PIC (Fig. 2). Taking into account differences in hyperfine structure, rotational partition function, and dipole moment, we estimate the abundance ratio of PIC to BN is approximately 0.05%, and is not particularly sensitive to experimental conditions, such as the discharge voltage or the precursor concentration. This finding is consistent with prior studies, but yields a direct and considerably more precise measurement of PIC production compared to earlier work.

As a check that the CN bond remains intact during BN formation, an identical experiment was performed using $CH_3{}^{13}CN$ as the precursor gas. As expected, equally strong lines of $C_6H_5{}^{13}CN$ were observed while those of other four ^{13}C isotopic species of BN were observed roughly at the intensity level expected from their natural abundance (1.3%), or, for the equivalent C atoms,

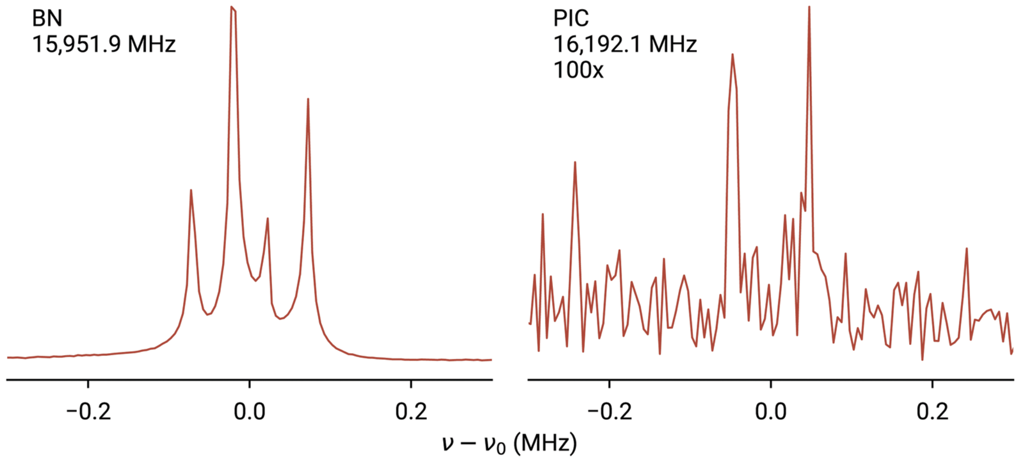

Fig. 2 Comparison of the relative intensities of the same rotational transition ($6_{0,6}$–$5_{0,5}$) of BN (left) and PIC (right), as observed by cavity FT microwave spectroscopy through a discharge starting with a dilute mixture of benzene and CH_3CN in Ne. At high spectral resolution, each transition is split into several hyperfine components owing to the I = 1 spin of ^{14}N, and is further split by Doppler doubling, an instrumental artifact that arises because the jet expands along the axis of the Fabry–Perot cavity. The same integration time (~3 min) was used for both spectra, but the PIC spectrum was recorded with an amplifier gain 100 times greater that used for the BN spectrum.

at twice this intensity. Furthermore, these results imply that the reactive partner with CN radical is almost certainly benzene, and not one of its higher-energy polar isomers such has fulvene and benzalene, since neither isomer is present in sufficient abundance in the absence of CN to account for the production of BN when a source of CN is added to the gas mixture.

Although less likely, it is also conceivable that phenyl radical (C_6H_5) might be produced in substantial quantities, and that BN is instead generated by the reaction:

$$C_6H_5 + CN \rightarrow C_6H_5CN \tag{6}$$

Trevitt *et al.* also considered the possibility that benzene + CN yields C_6H_5 + HCN. However, rotational lines of phenyl radical are also known,[44] and subsequent searches revealed no evidence of this radical under conditions that produce strong BN signals, circumstantial evidence that neither reaction (6) nor the C_6H_5 + HCN product channel are important in our experiment. Because reaction (6) is an exothermic, barrierless radical–radical recombination reaction, with no energetic barrier with respect to either product channel, both BN and PIC should be produced in approximately equal amounts, in direct contradiction to our experimental findings.

Quantum chemical calculations performed here reveal that not one but two energetic barriers must be surmounted for reaction (3) to produce PIC, while BN occurs highly exothermically and barrierlessly *via* reaction (2). For this reason, the former product channel should be inefficient at the low temperatures in the ISM, and will likely affect the product ratio in the laboratory experiments (and certainly in space). If reaction (2) is the dominant mechanism in our molecular source, there should be a strong propensity for BN over PIC, in accordance with our (and other) observations. We thus conclude that BN production in our experiment is both prompt and direct, proceeding almost exclusively *via* reaction (2). Given the wide array of experimental approaches that have now been brought to bear on the reaction between benzene and CN radical, and the consistency of the findings, we conclude with considerable confidence that BN is an excellent observational proxy for benzene, both in the laboratory and in the ISM.

4.3 Evidence for benzene formation *via* reaction (1)

Since reaction (1) appears to be a promising pathway to form benzene in the cold ISM, laboratory experiments were undertaken to test the hypothesis that benzene formation can be inferred *via* its subsequent reaction with CN, *i.e.* reaction (2). Although neither the precursor (*trans*-butadiene) nor the ring product (benzene) in the reaction (1) possesses a microwave spectrum, reaction (2) proceeds facilely to yield a highly polar species with a distinctive rotational signature. Butadiene was synthesized in high yield by the reduction of 1,4-dichlorobutyne,[45] while C_2H radical can be readily produced by discharging a variety of hydrocarbon precursors. Because reaction (5) yields C_2H in addition to CN radical, however, HC_3N is the ideal precursor choice: according to Fig. 1, the former radical is required in reaction (1) to produce benzene, while the latter is needed in reaction (2) to generated BN. Hence, only two precursors, butadiene and HC_3N, in theory are needed to generate BN.

As before, a discharge was applied to a gas mixture of HC_3N and $CH_2(CH)_2CH_2$ heavily diluted in Ne carrier gas, with the products detected by cavity FT microwave spectroscopy. Under these conditions, lines of BN were readily observed, implying production of benzene followed by BN. It is conceivable, however, that other pathways might be operative in our discharge source. The most obvious one is a Diels–Alder-type reaction between HC_3N and $CH_2(CH)_2CH_2$ to produce BN directly (forgoing benzene) *via*:

$$HC_3N + CH_2(CH)_2CH_2 \rightarrow C_6H_5CN + 2H, \tag{7}$$

where $CH_2(CH)_2CH_2$ presumably must adopt a *cis* configuration to proceed with the conventional 4+2 cyclization. To eliminate this possibility, HC_3N was replaced with CH_3CN and acetylene (C_2H_2) in the gas mixture at roughly the same stoichiometric ratio. Again, lines of BN were observed, albeit with somewhat lower intensity. This intensity decrease likely arises from unequal quantities of the two radicals (CN and C_2H) when each is produced from a different precursor, as opposed to equal quantities when using the same precursor (HC_3N). The production of BN using both precursor mixtures combined with the greatly reduced concentration of HC_3N using the latter gas mixture, again points to the importance of benzene as an intermediate in the pathway to BN.

The benzene abundance in the $CH_2(CH)_2CH_2/CH_3CN/C_2H_2$ discharge has been estimated by comparing the BN intensity to that observed in the benzene/CH_3CN experiments, since the BN intensity in the latter experiment linearly depends on the benzene concentration, which is known accurately. By simply replacing $CH_2(CH)_2CH_2/CH_3CN$ with benzene using otherwise identical experimental conditions, we estimate that of order 8×10^{11} benzene molecules are produced in the reaction between $CH_2(CH)_2CH_2$ and C_2H_2.

Additional calculations were performed to sample the potential energy surface for reaction (7); the resulting surface is shown in Fig. 4. Since *cis*-butadiene is required for the conventional 4+2 cycloaddition to proceed, formation of the 1,4-cyclohexadiene-1-carbonitrile adduct requires surmounting a 76 kJ mol^{-1} barrier. The loss of two additional hydrogen atoms yields BN, which can occur in either in a concerted or stepwise fashion. In addition to requiring a large amount of additional energy, this mechanism is unable to explain the formation of (trace) PIC, which was also observed. For these reasons, we conclude that this direct cycloaddition process does not contribute significantly to the BN observed in our experiment, and instead the operative reactions are the formation of benzene (reaction (5)) followed by reaction (1).

In the context of the reaction between 1,3-butadiene and C_2H, the crossed-molecular beam study by Jones *et al.*[22] and photoionization mass-spectrometry by Lockyear *et al.*[36] found evidence for different C_6H_6 products: the former found evidence for benzene (40%), while the latter concluded fulvene was a major product (57% ± 30%). In this work, we provide a different perspective on this reaction as microwave spectroscopy affords

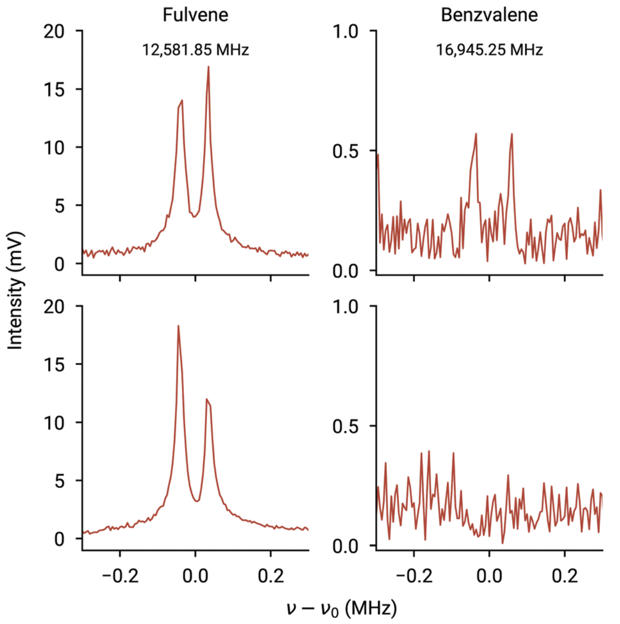

Fig. 3 Evidence for two high-energy polar C_6H_6 isomers in a benzene (top row) or butadiene/HCCH (bottom row) discharge. Fulvene and benzvalene were monitored *via* their a-type $J = 2_{02}–1_{01}$ and $2_{12}–1_{11}$ transitions, respectively. Each spectrum is the result of ∼3 min of integration.

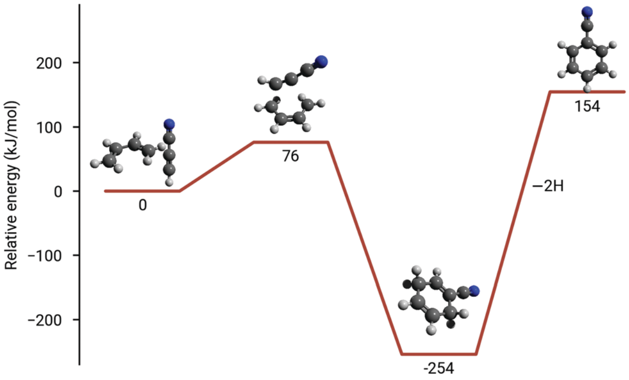

Fig. 4 G3//B3LYP potential energy surface for the 4+2 cycloaddition of *cis*-butadiene and HC_3N, and subsequent loss of two hydrogen atoms to yield BN. Energies are relative to the reactant asymptote. Barriers to hydrogen loss by the adduct are omitted.

isomer-specific detection of polar species; we have also searched for evidence of several higher-energy, polar C_6H_6 isomers whose microwave spectra have been previously reported: fulvene,[46] the second most stable most stable isomeric arrangement of C_6H_6, predicted to ∼130 kJ mol^{-1} less stable than benzene,[47] and benzvalene[48,49] which is about 170 kJ mol^{-1} less stable than fulvene. We have done so in the absence and presence of a CN source. In the absence of CN, lines of fulvene are easily observed (Fig. 3), while no evidence was found for benzvalene. The mere presence of fulvene under these conditions provides direct evidence that cyclization processes are efficient at some level, and strongly imply, independent of other information, the likely presence of its far more stable isomer—benzene—in our discharge nozzle source. By comparing line intensities to that of a molecule at a known fractional abundance (0.5% OCS in He), and taking into account differences in rotational partition function and dipole moment, the fulvene abundance is estimated to be 4×10^{11} molecules per gas pulse, *i.e.* the same order of magnitude derived for benzene under nearly identical conditions, but by an independent method. Furthermore, the fulvene line intensities are unaffected when a source of CN radicals is added to the discharge mixture, implying another reactant must be present so as to produce BN. From these observations, we infer that reactant to be benzene.

As indicated in Fig. 3, when the production of the two high-energy, polar C_6H_6 isomers is compared with a discharge of benzene *versus* $CH_2(CH)_2CH_2/C_2H_2$, fulvene is produced at a similar abundance with either precursor combination, but evidence is only found for benzvalene with benzene. In the former experiment, isomer abundance and relative stability are well correlated. This behavior almost certainly reflects the role of electrons which impart enough energy *via* collisions (typically several eV) to overcome isomerization barriers, and thereby produce higher-energy isomers in rough proportion to isomeric stability. Similar behavior has been observed in other isomeric systems.[50] Under our experimental conditions, the fulvene abundance is roughly 0.01% that of benzene, while the benzvalene to benzene ratio is about an order of magnitude lower. The selective production of fulvene relative to benzvalene in the latter experiment instead reflects the importance of different product channels, a finding which is further amplified by the production of the benzene and fulvene in comparable abundances. Owing to uncertainties arising from a highly-variable, frequency-dependent instrument response function, however, it is not possible to more precisely quantify the relative product yield of benzene *versus* fulvene.

While $CH_2(CH)_2CH_2$ has been incorporated into astrochemical networks,[51] it has not been detected in the ISM to date. This absence is almost certainly a consequence of its symmetry and therefore lack of a dipole moment, which, like benzene, precludes detection with ground-based radio telescopes. Its higher-lying *gauche* isomer is polar, but with a vanishingly small dipole (0.09 D),[35] making it an extremely challenging target for radioastronomical detection, since the detection sensitivity is proportional to the square of the dipole moment.

4.4 Evidence of benzene formation from known interstellar molecules

To explore the formation of benzene further, we then sought to generate it by starting with known interstellar molecules. Diacetylene (HC_4H) was first reported in the ISM using the Infrared Space Observatory,[10] and more recently by observation of rotationally-resolved vibrational transitions in IRC + 10216.[52] Although speculative, the reaction of C_2H_2 with hydrogenated HC_4H may form C_6H_6 *via* a reaction of the type:

$$C_2H + HC_4H \xrightarrow{H} C_6H_6. \qquad (8)$$

Similar reactions has been invoked in the formation of C_6H_6 in combustion environments, but there is disagreement in the literature as to the efficiency of product formation.[53,54]

Nevertheless, to test this pathway, a discharge was applied to a dilute mixture of HC_3N and HC_4H in Ne, and strong lines of BN were observed. Although we can not be certain of the mechanism that is operative, BN detection suggests that reaction (8) may be viable pathway to form benzene. Based on the combustion models, it appears that HC_4H first undergoes hydrogenation to produce $CH_2(CH)_2CH_2$ or in a more complex sets of steps, the C_4H_x (x = 3, 5) radical followed by reaction with acetylene forms phenyl radical, and ultimately benzene by H addition. Circumstantial evidence in support of hydrogen addition, which is necessary in either pathway, is that discharge experiments starting with unsaturated carbon chains such as HC_4H alone are known to produce methyl-terminated chains, such as CH_3C_4H,[55] suggesting that some degree of hydrogenation occurs facilely under our experimental conditions.

Motivated by this finding, C_2H_2 was tested, since this molecule is a far more widespread and common interstellar species compared to HC_4H.[56] Indeed, even when starting with this simple precursor (along with HC_3N, both diluted to 1% in Ne), weak lines of BN were observed in the presence of the discharge. Owing to the number of reactions that must take place to eventually form benzene and the low yield of BN, it is not possible to put forth a meaningful reaction pathway. It is plausible, however, that a major pathway proceeds through HC_4H formation:[57]

$$C_2H + C_2H_2 \rightarrow HC_4H + H. \tag{9}$$

In this scenario, benzene could subsequently be produced *via* reaction (8), by reaction with a second C_2H radical, probably from C_2H_2 or *via* reaction (5).

5 Discussion

Microwave spectroscopy has many practical advantages in the study of formation pathways and branching ratios.[58,59] Because of its intrinsically high spectral resolution and sensitivity, it is straightforward to differentiate between isomers and isotopic species, and to determine abundances even if the products are present at low concentration, since this quantity can be inferred from the intrinsic line strength, rotational partition function, and dipole moment. Although the experimental conditions used here do not replicate the very low temperature and pressure in a dark molecular cloud such as TMC-1, the present work may provide insight into the basic chemical pathways that are operative there, and possible products, since the feedstock for the experiments are known astronomical molecules (with the exception of $CH_2(CH)_2CH_2$), and application of an electrical discharge generates a wealth of species, many of which have also been identified in this astronomical source.

With respect to BN specifically, the work here further amplifies conclusions drawn from elegant prior crossed-molecular beam and kinetic studies. The reaction of benzene + CN is found to produce BN in high yield, with scant yield of its high energy PIC isomer; isotopic measurements confirm that the CN bond remains intact during molecule formation. Supported by high accuracy chemical calculations and previous theoretical studies, we conclude that BN can be used as a reliable tracer for the presence of benzene, since all experimental and theoretical evidence points to a barrierless, exothermic reaction to form this isomer, with a vanishingly small branching fraction forming PIC. The ability of chemical models to reliably reproduce the majority of the observed interstellar BN abundance[8] using reaction (2) lends further support to this argument. Finally, an examination of the observational data from McGuire *et al.*[8] shows no evidence of signal from PIC, although the noise levels prevent the establishment of an upper limit as robust as that seen in the laboratory. Further observations are planned to quantitatively explore this reaction pathway in TMC-1.

Beyond benzene as a precursor, experiments performed with smaller and simpler hydrocarbons, ranging from $CH_2(CH)_2CH_2$ to HC_4H and even C_2H_2, in the combination with HC_3N, consistently found evidence for BN. Because a number of reactions presumably must take place to synthesize benzene from smaller hydrocarbons, it is not possible to infer with confidence the reaction pathways there are operative in the laboratory, and therefore whether these are also realistic in the ISM. Nevertheless, they do suggest that follow-up laboratory studies examining the efficiency, kinetics, and product channels involving reactions of these hydrocarbons under single-collision conditions are warranted. If viable in space, developing a quantitative relationship between simpler precursors and C_6H_6 would be particularly valuable.

Because lines of fulvene are readily detected in a $CH_2(CH)_2CH_2/C_2H_2$ discharge, it would be surprising if other isomers, specifically acyclic chains such as 1,3-hexadien-5-yne, can not eventually be spectroscopically characterized by the same approach employed here. Although a major impediment to microwave detection is their low calculated dipole moments ($\sim$0.1 D), line intensities in FT microwave spectroscopy scale as μ, not as μ^2 as in conventional absorption or emission spectroscopy, which enables weakly polar molecules to be more easily detected by this method.

As previously emphasized by Lockyear *et al.*,[36] an astronomical search for fulvene may be worth pursuing. The discovery of BN in TMC-1 implies the presence of benzene, and if produced *via* reaction (1), it appears from the work here and previously[36] that this high-energy isomer may be an important byproduct. Fulvene is modestly polar (0.42 D) and its low-frequency rotational lines[46] were measured some time ago, so there is no obvious obstacle that would preclude a search. As with BN, the first step may be to average spectra from a published spectral line survey[60] to establish whether there is any promising evidence for this isomer. As with BN, it may prove fruitful to search for cyanide-substituted fulvene analogs. As shown in Fig. 5, three isomers lie very close in energy, and are only 120 kJ mol^{-1} less stable than BN. Furthermore, they are highly polar, with dipole moments comparable in magnitude with BN (4.51 D).[61] B3LYP/6-31G(d) calculations predict that each possesses a significant dipole moment along the a-inertial axis ($\sim$4 D) and a smaller one along the b-axis ($\sim$0.8 D).

The synthesis of BN, and by inference benzene, from small hydrocarbon precursors in the laboratory experiments suggests

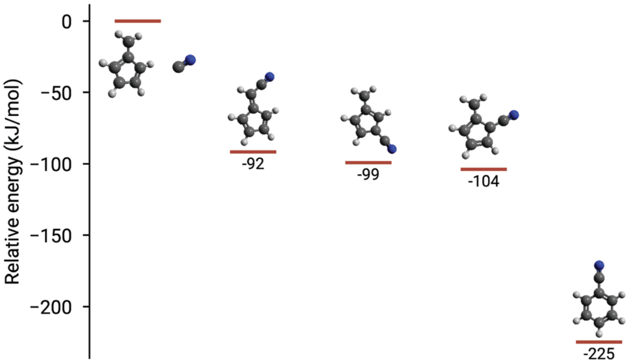

Fig. 5 Relative energies of the three cyanide-substituted fulvene derivatives. Energies are given relative to the fulvene + CN radical asymptote, in kJ mol^{-1}.

the transition from acyclic to cyclic carbon structures is facile, implying that still larger aromatic molecules may be detectable by similar means. Although preliminary searches for rotational lines of small, polar PAHs such as azulene and acenaphthene were unsuccessful,[62] this failure may simply be a consequence of the relatively short reaction time in the discharge nozzle. Production of long-chain cyanopolyynes such as $HC_{15}N$ and $HC_{17}N$ required use of a nozzle source with a longer reaction channel,[63] presumably because the larger number of collisions prior to adiabatic expansions shift the chemistry to larger, more complex molecules.

The present work suggests a renewed astronomical search for $CH_2(CH)_2CH_2$ is worth pursing. It is in fact the only precursor used in our experiments which has yet to be detected in space. Like C_6H_6, astronomical detection will almost certainly require a space-based or extremely high-altitude facility. The infrared spectrum of the ground state *trans* isomer has been extensively studied by Craig and co-workers.[64] Among its many infrared active modes, the strongest one free from telluric contamination lies near 11 μm.

There is considerable debate in the literature[65–68] as to the formation routes of PAHs and their fullerene cousins, specifically interstellar C_{60}, C_{70}, and C_{60}^+ (ref. 69 and 70). This debate centers on the relative importance of 'bottom-up' *versus* 'top-down' in molecule formation, *i.e.* are these large organic molecules formed from sequential reactions of smaller molecules (bottom-up) or from the degradation of still larger molecules (or small grains) synthesized in AGB stars and supernovae (top-down). While the top-down mechanism appears to have gained favor in recent years to rationalize the abundance of large PAHs and fullerenes, the detection of BN in TMC-1 indicates that bottom-up synthesis is viable, at least for smaller aromatic molecules. Because this source is a cold, dark, starless cloud with quiescent conditions, it is highly unlikely that its chemistry is dominated by the degradation of large PAHs or carbonaceous macromolecules/dust. Rather, TMC-1 has an rich inventory of small, reactive hydrocarbon species[71] like those implicated here to produce BN in the laboratory. If reactions involving these species are indeed efficient at the density and pressure of TMC-1, chemical models can be calibrated and used to explore the relative importance of this bottom-up chemistry to aromatic molecule and PAH formation in a far wider range of astrophysical environments.

6 Conclusions

A microwave and theoretical study exploring the utility of benzonitrile (BN; C_6H_5CN) as an observational proxy for benzene (C_6H_6) has been presented. The primary conclusions of this work are:

(1) The G3//B3LYP composite thermochemical calculations provide a self-consistent and accurate set of energetics linking the cyclization of butadiene and C_2H to the formation of BN and PIC from C_6H_6 + CN. The new calculations have been used to rationalize experimental observations, and should prove useful for subsequent chemical modeling.

(2) BN formation occurs *via* the radical–neutral reaction of CN with benzene, rather than *via* a radical–radical reaction of CN with phenyl radical (C_6H_5). The presence of BN is therefore a good observation proxy for benzene.

(3) The presence of benzene has been inferred in an electrical discharge starting with 1,3-butadiene ($CH_2(CH)_2CH_2$) and precursors which are known to produce C_2H radicals. Direct spectroscopic evidence is also found for fulvene, a well-studied, high-energy polar isomer of benzene under the same conditions, indicating that cyclization occurs at some level under our experimental conditions. Its steady-state concentration is comparable to that inferred for benzene by –CN tagging, implying that both cyclic isomers may be important products in this reaction. As such, these findings are consistent with earlier work of both Jones *et al.*[22] and Lockyear *et al.*[36] It should be emphasized, however, that the experimental conditions in all three studies are markedly different with respect to temperature, pressure, and density.

(4) Evidence was also found for BN when other hydrocarbons precursors such as diacetylene and even acetylene were used in place of 1,3-butadiene, suggesting that cyclic, aromatic carbon structures can be readily generated from acyclic precursors. In light of these findings, efficiency and kinetics of reactions involving these species under single-collision conditions should be studied in greater detail.

(5) Detection of BN in the cold, starless dark cloud TMC-1 where many small molecules are abundant is strongly indicative that efficient 'bottom-up' aromatic chemistry is operative in some interstellar environments.

7 Note added to manuscript

Following submission of this paper, the rotational spectra of the aforementioned acyclic 1,3-hexadien-5-yne isomers (both *E* and *Z* conformers) have been detected; measured line frequencies and best-fit spectroscopic constants will be summarzied in a subsequent publication.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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