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Prediction and Rationalization of Abundant C−N−H Molecules in Different Environments

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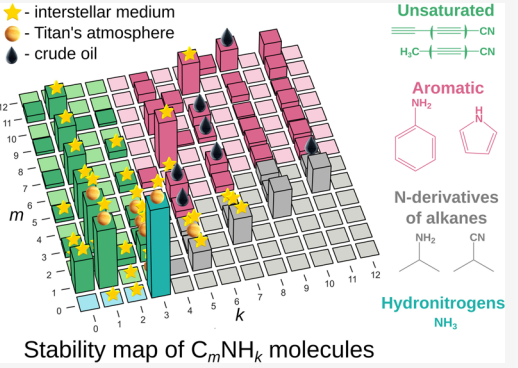
ABSTRACT: The extreme chemical diversity of $C_mN_nH_k$ molecules is at the same time very important (central in organic chemistry) and difficult to rationalize in the sense that some molecules are abundant and easy to synthesize, while others are rare and difficult to make. Using the recently developed criteria of molecular "magicity", combined with evolutionary structure prediction and quantum-chemical calculations, we study these molecules in a wide range of compositions ($0 \le m \le 13$, $0 \le n \le 4$, and $0 \le k \le 14$). "Magic" molecules are defined as those that are lower in energy than any isochemical mixture of molecules with the nearest compositions. The predicted "magic" molecules are in good agreement with compounds found in versatile environments (interstellar and circumstellar media, Titan's lower atmosphere, and crude oil fractions) and in experimental chemistry. This work shows the predictive power of our approach, capable of predicting and explaining stable molecules in complex systems.



Stability map of C_mNH_k molecules

All organic compounds can be viewed as derivatives of hydrocarbon (C−H) molecules, and recently we showed[1] how, using the notion of "magic" molecules (borrowed from studies of nanoparticles and atomic nuclei), one can explain the wide variety of hydrocarbons, their homologous series, ease or difficulty of synthesis, and reactivity. This not only explained known facts but also put them into a new perspective, giving a simple and powerful systematics. Increasing chemical complexity by adding nitrogen and oxygen atoms will significantly increase the computational complexity of the study and also bring us closer to understanding the full landscape of organic chemistry and perhaps the chemistry and origins of life. Here we add nitrogen and consider the C−N−H system.

C−N−H molecules are known in great variety and constitute one of the fundamental organic systems. This system is present in very diverse environments, from interstellar space to planetary atmospheres and petroleum fields. The discovery of space molecules containing nitrogen has a long history. With the invention of rotational spectroscopy, the cyano-radical was one of the first detected binary molecules in interstellar medium in 1940[2] and NH_3 was the first "big molecule", having more than two atoms discovered in 1968 by the Townes group.[3] To date, many more interstellar and circumstellar molecules have been found, and the search continues, highlighting the challenge of rationalizing their stability: why are these molecules present and others are not?

Another interesting environment known for versatile organic nitrogen compounds is the lower atmosphere of Titan (the largest satellite of Saturn).[4] Just like the Earth's atmosphere, the atmosphere of Titan is predominantly composed of nitrogen. Various nitrogen-containing molecules have been found in Titan's lower atmosphere, including radicals (NH), dinitriles (C_2N_2, C_4N_2),[5] such aromatic compounds as 2,4-diazaphenanthrene $C_{12}N_2H_8$,[6] and other aliphatic molecules. Under UV irradiation and electric discharges, these molecules produce tholins (previously known as "intractable polymers" because of their poorly defined structures and compositions), which give Titan's atmosphere its orange color.[7] It is likely that similar molecules were present in the atmosphere of the early Earth, before free oxygen appeared (some 2−2.5 billion years ago) and oxidized such molecules.

Cyclic $C_mN_nH_k$ compounds are present in crude oil, where they constitute up to 10 wt %[8]—mostly, these are heterocyclic compounds, which are very common constituents of synthetic organic materials. They can be considered chemically stable due to many effects: induction, mesomeric effect, and of course, aromaticity.

Likewise, there is a need to understand nitrogen-containing molecules appearing in experiments. Some molecules are easily synthesized under mild conditions, in the pure C−N−H system, without special precursors or catalysts, and can in turn

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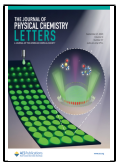

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be used as precursors of many other organic compounds. Such molecules could be considered to be highly stable. Other molecules are difficult to make under mild conditions with a high reaction yield.

Important and unresolved issues are why some $C_mN_nH_k$ molecules are found in different environments with high concentrations and can be easily synthesized, while others are rare or absent in nature, and are difficult to make in the laboratory without special precursors. Conducting experiments to answer these questions is extremely difficult, while detailed theoretical calculations require huge computing resources. So, in the work of Etim et al.,[9] chemical modeling was performed for small C_mN and C_mNH molecules in dense and translucent clouds, but this entailed calculation of reaction pathways and rate coefficients (see ref 9). Mebel et al. studied formation processes of larger molecules present in interstellar medium, planetary atmospheres, and combustion flames.[10−13] This included the calculation of reaction pathways and kinetic barriers for various compounds, e.g., polyaromatic hydrocarbons. However, there are much simpler and less quantitative but more general approaches based on energy variance of investigated molecules. Some researchers attempted to connect the presence of molecules in the interstellar medium with the enthalpies of formation of these molecules.[9] For example, C_mNH molecules with an odd number of carbon atoms are found to be more stable than even-numbered ones. This is consistent with the existence of long-chain C_mNH molecules with odd m values in the interstellar medium. Also, experimental methods can be employed to assess stability, for example, by evaluating the ease of synthesis, as well as reactivity and propensity to degradation of the substance.

In our previous works[14−18] we elucidated the stability of the clusters and molecules using criteria that showed great success in the studies of nanoparticles and atomic nuclei (which, like molecules, are finite metastable aggregates of particles). These criteria are based on second-order energy differences and fragmentation energies. Here we apply the same methodology to ternary organic N-containing molecules and compare predictions with the compounds found in the interstellar medium, Titan's atmosphere, and oil fractions.

II. COMPUTATIONAL METHODOLOGY

Structures of $C_mN_nH_k$ molecules in a wide compositional area were found using our recently developed variable-composition global optimization algorithm for molecules and nanoclusters,[14] implemented in the USPEX code.[19,20] This method takes advantage of exchange of structural fragments between clusters of different compositions, which accelerates structure prediction by ∼5 times for unary and ∼50 times for binary systems compared to the conventional techniques that perform global optimization separately for each cluster's composition.

To maximize efficiency and reliability, structure prediction consisted of three stages. In the first stage we performed the USPEX search at the semiempirical level of theory, using PM6 and PM7 approximations, as implemented in the MOPAC code.[21] The second state consisted of recalculating the obtained structures using density-functional code VASP,[22,23] using the projector augmented wave method[24] and spin-polarized PBE exchange−correlation functional.[25] In the final stage, for each composition we selected 10 lowest-energy (at PBE level of theory) isomers and refined their structures and energies using the B3LYP hybrid functional and 6-311+G(d,p) basis set, as implemented in the GAUSSIAN code.[26]

Regarding the stability of ternary molecules $C_mN_nH_k$, we use two criteria, elaborated in our previous studies,[1,14] based on the ground-state energies $E(m, n, k)$ of molecules. In the first criterion, we consider stability with respect to exchange of a certain fragment (X) between two identical molecules $C_mN_nH_k$. In the general case, if the fragment X consists of x_1 C atoms, x_2 N atoms and x_3 H atoms, the energy change can be written as

$$\Delta^2_X E(m, n, k) = 1/2[E(m + x_1, n + x_2, k + x_3) + E(m - x_1, n - x_2, k - x_3) - 2E(m, n, k)] \quad (1)$$

which indicates how much more stable the given molecule with respect to the average energy of nearest (in compositional space) molecules and is a discrete analogue of the second derivative of the energy with respect to composition. Positive sign of $\Delta^2_X E$ means stability with respect to the exchange of the X fragment, while negative $\Delta^2_X E$ indicates the tendency toward "disproportionation" into compositions with +X and −X. Ordinarily, we consider the exchange of only individual atoms, that is, X = {C, N, H}, and quantify stability of the molecule by the minimum of corresponding energy changes: $\Delta^2_{min} = \min\{\Delta^2_C E, \Delta^2_N E, \Delta^2_H E\}$. In this study, we extended this criterion by allowing the exchange of diatomic N_2 and H_2 molecules, because the exchange of fragment with an even number of electrons is more favorable. We successfully used the same philosophy in our previous work on C−H molecules.[1] Thus, in our case, X = {C, N, H, 2N, 2H}, and the resulting formula for stability is as follows:

$$\Delta^2_{min} = \min\{\Delta^2_C E, \Delta^2_N E, \Delta^2_H E, \Delta^2_{2N} E, \Delta^2_{2H} E\} \quad (2)$$

Molecules with positive Δ^2_{min} are particularly stable and called "magic", by analogy with magic nanoclusters and magic nuclei (in nanoscience and nuclear physics).

We use one more criterion of stability, characterizing the resistance to fragmentation. For this purpose, we consider all possible fragmentation channels for the decomposition into two fragments:

$$C_mN_nH_k \rightarrow C_aN_bH_c + C_{m-a}N_{n-b}H_{k-c}, \quad \text{where } 0 \le a \le m, 0 \le b \le n, 0 \le c \le k \quad (3)$$

The energy of each fragmentation reaction is found as

$$E_{frag}(m, n, k, a, b, c) = E(a, b, c) + E(m - a, n - b, k - c) - E(m, n, k) \quad (4)$$

We are looking for the decomposition into the most stable fragments; hence, we calculate the minimum value of all fragmentation energies:

$$E_{frag}(m, n, k) = \min_{a,b,c} E_{frag}(m, n, k, a, b, c) \quad (5)$$

This criterion also has direct analogy in nuclear physics, where the energy of fragmentation indicates the fissibility of a nucleus.

Molecules that exhibit a positive value of Δ^2_{min} tend to be favored in the formation processes. Then, if a molecule has a negative E_{frag}, its concentration will gradually decrease due to decomposition. Consequently, over time, molecules that meet both criteria will dominate.

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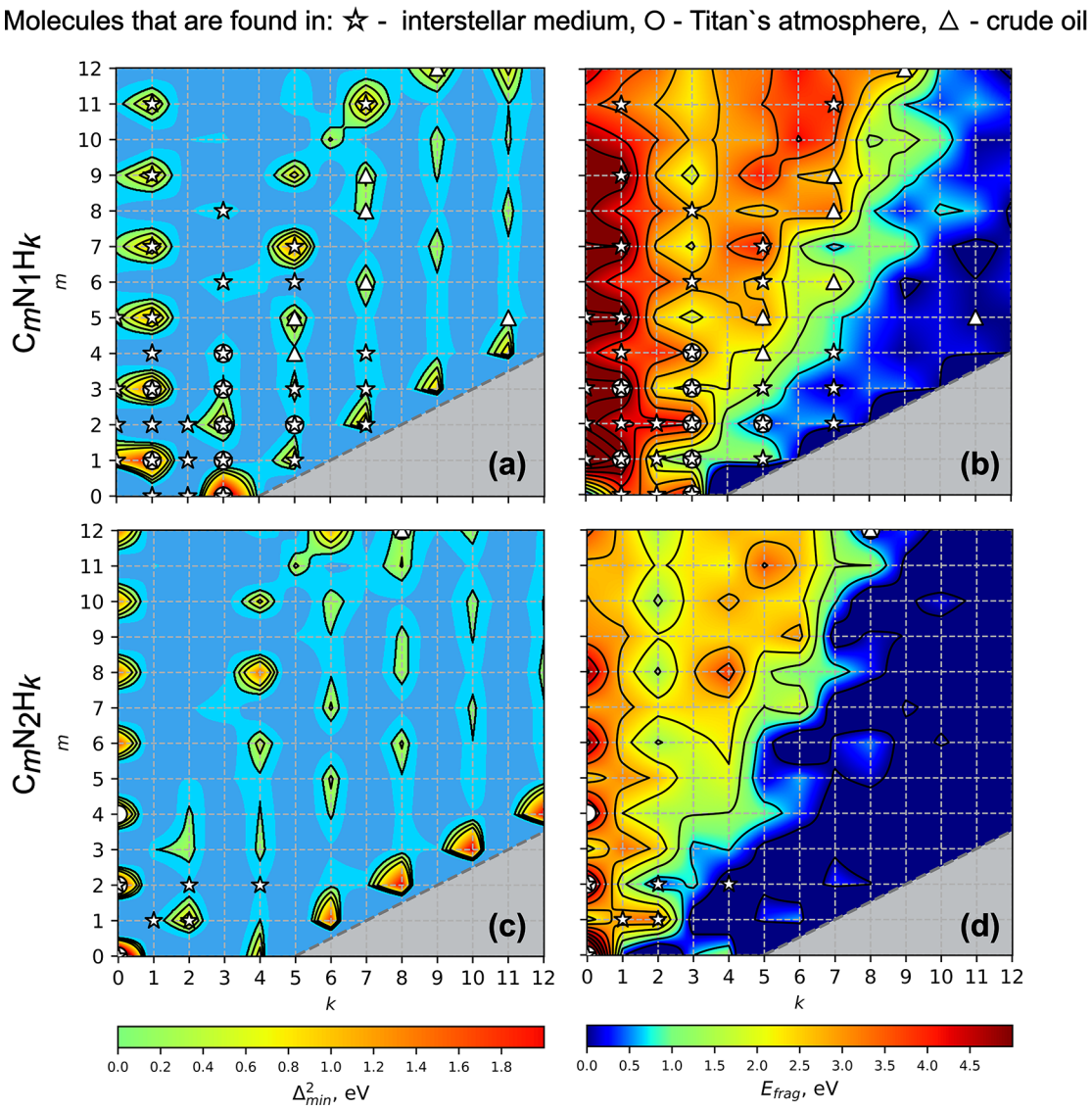

Figure 1. Stability maps of $C_mN_nH_k$ molecules (n = {1,2}) using two criteria: (a,c) $\Delta^2_{min}(m,n,k)$ and (b,d) $E_{frag}(m,n,k)$.

Additionally, we have used a third criterion, the HOMO−LUMO gap. Figure S1 shows interpolated heatmaps of gaps for $C_mN_nH_k$ molecules (n = {1,2}). This characterizes electronic polarizability of a molecule and its reactivity. Narrow gaps lead to lower reaction barriers; therefore, $C_mN_nH_k$ molecules with small HOMO−LUMO gaps usually have lower kinetic stability.

Ground-state structures of $C_mN_nH_k$ molecules were found in a vast compositional area of $0 \le m \le 13$, $0 \le n \le 4$ and $0 \le k \le 2m + 2n + 2$, which includes 1050 different compositions ($14 \times 15 \times 5$). Molecules with excess hydrogen ($k > 2m + 2n + 2$) are all unstable, have disjoint molecular graphs (i.e., are not single molecules), and are of no interest here. Table S1 gives the list of molecules detected in nature (in interstellar space, in Titan's atmosphere, and in crude oil), including their isomers. Their measures of stability (Δ^2_{min}, E_{frag}, HOMO−LUMO gaps and fragmentation channels) and Cartesian coordinates are also given in the Supporting Information. Space molecules are found usually in their ground-state structures; however, there are cases of the existence of several first isomers (CNH, CNH_2, CN_2H_2, C_2NH_3, C_2NH_5, C_3NH, C_3NH_3, C_3NH_4, C_5NH, C_6NH_5). For example, C_2NH_3 is found in three structural forms: acetonitrile, ketenimine, and methyl isocyanide, which are the ground-state, second-lowest, and third-lowest energy isomers, respectively. Further in this study we will focus mostly on ground-state structures for each composition.

According to the fragmentation energies and paths from Table S1, $C_mN_nH_k$ molecules with 2 or more nitrogen atoms demonstrate a propensity to decompose into N_2 and C_mH_k molecules. This is explained by the strong binding in molecular nitrogen; hence, the concentration and diversity of interstellar C_mNH_k molecules are significantly higher compared to $C_mN_2H_k$ (31 and 6 species), while molecular systems with 3 or 4 nitrogen atoms are practically absent in outer space.

Figure 1 presents heatmaps interpolating the calculated values of $\Delta^2_{min}(m,k)$ and $E_{frag}(m,k)$ for $C_mN_1H_k$ and $C_mN_2H_k$ molecules. Maps of Δ^2_{min} (Figure 1 a,c) are given in coordinates of m and k. Red color indicates highly stable magic molecules; blue color represents unstable compositions ($\Delta^2_{min} < 0$). Light blue regions indicate molecules with moderately negative Δ^2_{min} (-0.4 eV $\le \Delta^2_{min} \le 0$), and we will call such molecules "near-magic". For such molecules, Δ^2_{min}

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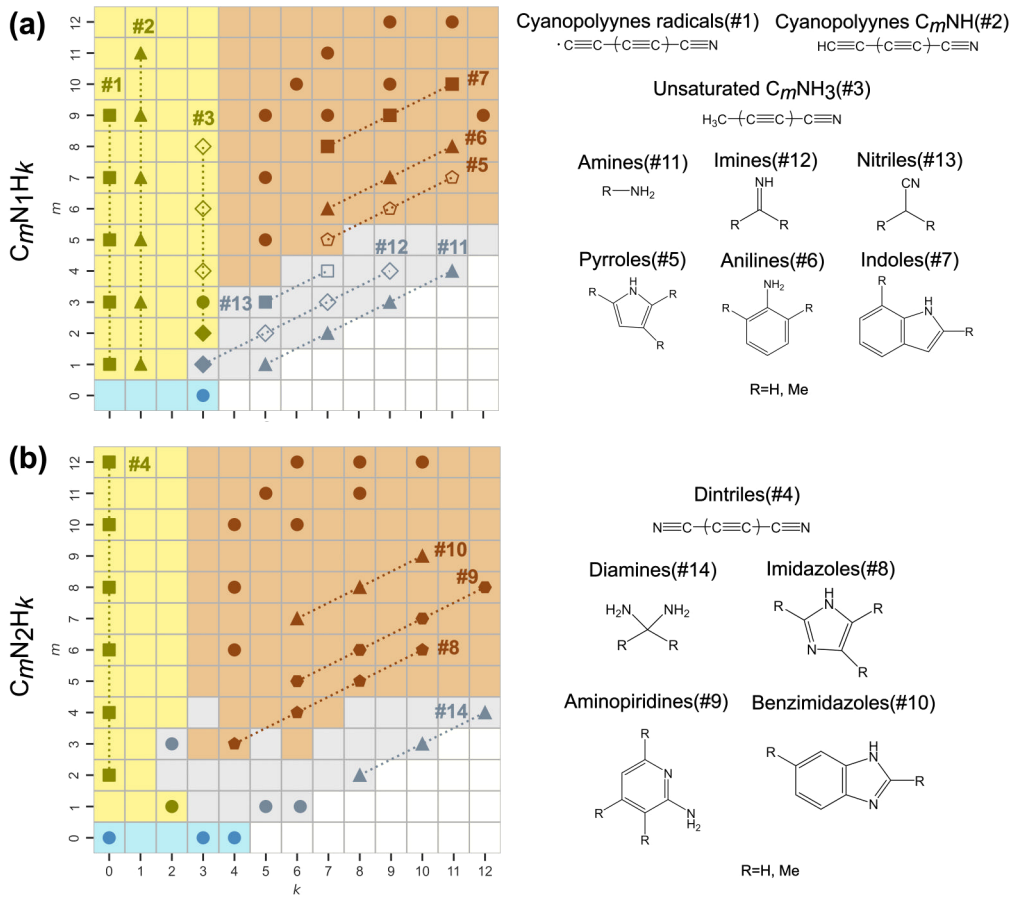

Figure 2. $C_mN_1H_k$ (a) and $C_mN_2H_k$ (b) molecules ($0 \le m, k \le 14$), divided into 4 classes: green for unsaturated structures, peach for aromatic compounds, gray for simple N derivatives of alkanes, and blue for pure hydronitrogens. Magic molecules are marked with filled symbols, near-magic molecules with slightly negative $\Delta^2_{min}E$ ($-0.4 \le \Delta^2_{min} < 0$) are marked with open symbols. Fourteen homologous series are identified and marked with different symbols.

can change sign at high temperature (or when more accurate theoretical approximations are used).

The maps of the fragmentation energy E_{frag} (Figure 1b,d) show areas of E_{frag} in the interval from 0 to 5 eV. Red regions of the map display the molecules exhibiting the presence of exceptionally strong bonds; it takes high energy to break them.

At first glance at the stability maps, one can see the most fundamental N-containing organic molecules: N_2, NH_3, C_2N_2 (cyanogen), N_2H_2 (hydrazine), CNH_5 (methylamine), C_6NH_7 (aniline), and $C_4N_2H_4$ (pyrimidine). They are present in planetary atmospheres and within biological entities and serve as precursors of biomolecules.

In all maps of Figure 1 we marked by special symbols the N-containing molecules found in interstellar and circumstellar media, in Titan's atmosphere, and in crude oil. All of these molecules are represented in Figure 3 and will be discussed below.

In the following discussion, we divide stable $C_mN_nH_k$ molecules into five classes based on their structural features: (1) unsaturated C−N−H compounds and all C−N molecules belong to this class, (2) aromatic compounds, or arenes (cyclic compounds with conjugated double bonds), (3) N derivatives of alkanes (saturated and unsaturated compounds without π-conjugation), (4) hydronitrogens, composed of only binary N_nH_k molecules, and (5) hydrocarbons, which form numerous homologous series and were discussed in detail in our recent work,[1] and for this reason will not be discussed here.

These classes are differently colored in Figure 2. For better insight, we present schematically all of the compositions of magic molecules in Figure 2, focusing on structural classes and homologous series. The homologous series are enumerated, labeled with different markers and displayed with a general skeletal formula. Below we provide a discussion of these molecules, starting with a consideration of the homologous series, as well as magic molecules that do not belong to any homologous series, in terms of their presence in various environments and experiments.

1. Unsaturated Compounds. Representatives of polyynes are divided into two groups, each of which has magic representatives: cyanopolyynes with one nitrogen and dinitriles with two nitrogens. The first series is the simple C_mN radicals (m = odd numbers up to 9), with linear structure and unpaired electron on the terminal carbon atom (#1, Figure 2). These molecules also have some of the highest values of fragmentation energy. CN,[2] C_3N,[27] and C_5N[28] molecules were indeed detected in interstellar medium. It is worth noting that C_mN molecules with even m show lower values of E_{frag} and negative Δ^2_{min} (for m = 2, −0.91; m = 4, −0.72; m = 6, −0.56; m = 8, −0.46; m = 10, −1.47; m = 12, −0.88 eV), which could be the reason for their absence in interstellar and circumstellar media. However, recently, the C_2N radical was registered in space.[29] Despite its $\Delta^2_{min} < 0$ (−0.91 eV), it has a higher value of E_{frag} (~5 eV) compared to other molecules belonging to group C_mN with odd m.

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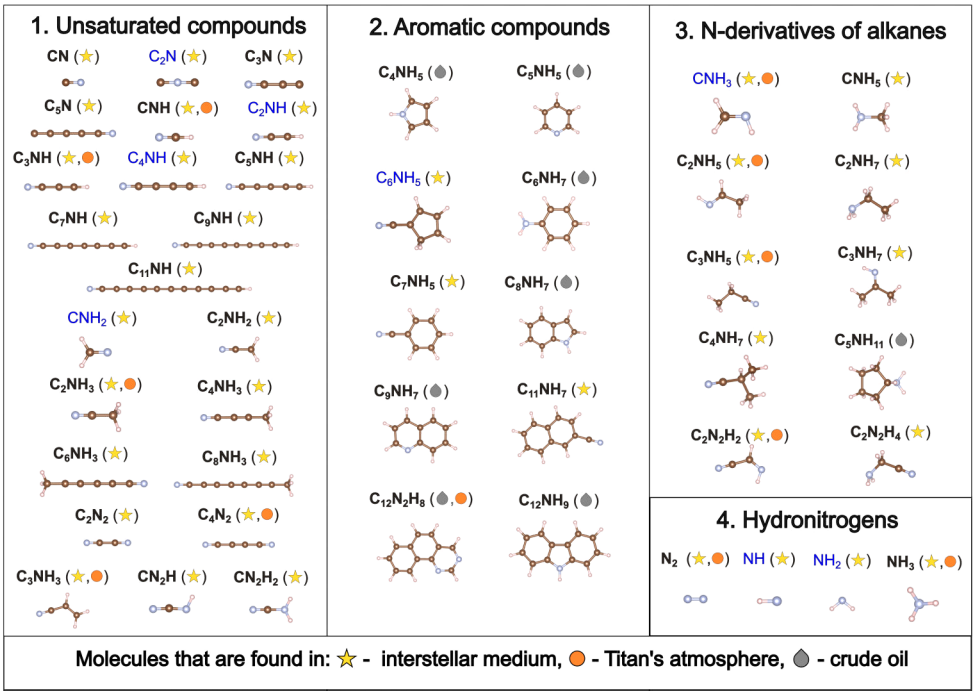

Figure 3. $C_mN_nH_k$ molecules are divided into four classes, unsaturated compounds, N derivatives of alkanes, and aromatic and hydronitrogens structures, that are found either in interstellar medium or in Titan's atmosphere or are components of crude oil. Nonmagic molecules are marked in blue.

The second series is C_mNH polyynes (m = odd numbers up to 11) (#2, Figure 2), which are similar to the previous group; however, the electron on the terminal C atom forms a bond with the H atom. These molecules have the highest magnitudes of Δ^2_{min} among all of the molecules considered here. All the molecules in this group were reported to be found in the space medium: prussic acid CNH,[30] C_3NH,[31] C_5NH,[32] C_7NH,[33] C_9NH,[34] and $C_{11}NH$.[35] Moreover, CNH and C_3NH were found in Titan's lower atmosphere. This is consistent with previous results:[9] enthalpies of formation of C_mNH molecules are higher for even m and lower for odd, forming a zigzag pattern, implying that the discovery of $C_{13}NH$ is more likely than that of $C_{12}NH$ or $C_{14}NH$. This is confirmed with values of the HOMO−LUMO gap: C_mNH molecules (m = even number up to 12) possess narrow gaps (Figure S1), which proves their high reactivity. C_2NH[36] and C_4NH[37] were registered in space too, unlike all other C_mNH molecules (m = odd number). The existence of C_2NH and C_4NH could be explained by availability of their precursors in the following formation mechanisms:[38]

$$C_2 + NH_3 \rightarrow [C_2{-}NH_3] \rightarrow H_3C_2N \rightarrow HC_2N + H_2$$

$$C_3 + HCN \rightarrow C_4NH$$

The third homologous series is polyynes with the generic formula C_mNH_3 (m = even numbers up to 8) (#3, Figure 2). They have linear structure with the cyano substituent on the terminal carbon atom and methyl on the other end. C_2NH_3 has positive Δ^2_{min} (0.64 eV), and C_4NH_3,[39] C_6NH_3,[40] and C_8NH_3[41] have small negative values of Δ^2_{min} (−0.12, −0.14, and −0.13 eV) and thus are classified as near-magic molecules. All these molecules are present in the interstellar medium and smaller molecules C_2NH_3 and C_4NH_3 are found also in Titan's dense clouds.[42]

Unsaturated compounds with two nitrogen atoms consist only of one homologous series of magic molecules, dinitriles C_mN_2 (m = even numbers up to 12) (#4, Figure 2). These molecules have high values of both E_{frag} and Δ^2_{min}. C_2N_2 is an interstellar molecule.[43] Furthermore, C_2N_2 and C_4N_2 were recently found in the atmosphere of Titan.[44]

CNH_2[45] and C_2NH_2[46] are radicals present in interstellar medium. Moreover, CNH_2 is found in two isomeric forms: methylene amidogen and aminocarbyne, which are the ground state and third isomer, respectively, in our calculations. These molecules have an odd number of electrons, the single unpaired electron being located on the nitrogen atom. They both have negative Δ^2_{min} (−1.24 and −0.15 eV), but positive E_{frag} (1.53 and 4.51 eV). The open-shell electronic structure makes these molecules highly reactive. CN_2H (cyanomidyl radical)[47] is another space radical that has a high fragmentation energy (3.31 eV) and a small negative Δ^2_{min} (−0.35 eV).

CN_2H_2 (Δ^2_{min} = 0.9 eV and E_{frag} = 3.5 eV) exists in the interstellar medium as two isomers: carbodiimide and cyanamide.[48] C_3NH_3 has the structure of cyanoethene (acrylonitrile). It is notable for being detected both in the interstellar medium[49] and in Titan's lower atmosphere.[50] Moreover, there is one more isomer of C_3NH_3 with the structure of propargylimine[51] that has been found in space and is the fourth isomer, 1.45 eV higher in energy than the ground-state structure.

2. Aromatic Compounds. Aromatic compounds contain one or several condensed carbon rings and can have different substituents and heteroatoms. The fifth homologous series that we highlight is pyrroles and their methylated derivatives (C_mNH_{2m-3}: C_5NH_7, C_6NH_9, C_7NH_{11}) (#5, Figure 2).

The sixth homologous series is anilines (C_mNH_{2m-5}: C_6NH_7, C_7NH_9, C_8NH_{11}) (#6, Figure 2). Anilines are aminobenzyls with one or two hydrogen atoms substituted by methyls in ortho patterns. Aniline and its alkyl derivatives are contained in

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high concentrations in products of thermal processing of oil at high temperatures.[8]

Indole or 2,3-benzopyrrole (C_8NH_7) and its derivatives 2-methylindole (C_9NH_9) and 2,5-dimethylindole ($C_{10}NH_{11}$) constitute the seventh homologous series with the general formula C_mNH_{2m-9} (#7, Figure 2). Indole itself is an important molecule, present in oil fractions[8] and used as a crucial precursor in organic synthesis with medical applications.[52] 2-methylindole (C_9NH_9) is an intermediate in the production of organic dyes.[53]

There are several homologous series containing two nitrogen atoms. The eighth series consists of imidazole ($C_3N_2H_4$) and its methylated derivatives ($C_mN_2H_{2m-2}$: $C_4N_2H_6$, $C_5N_2H_8$, $C_6N_2H_{10}$) (#8, Figure 2). The 1,3-diazole, $C_3N_2H_4$, has a 5-membered ring containing two nitrogen atoms, and having the aromatic sextet of π-electrons. The ninth homologous series (#9, Figure 2) is comprised of aminopyridines $C_mN_2H_{2m-4}$: $C_5N_2H_6$, $C_6N_2H_8$, $C_7N_2H_2$, and $C_8N_2H_{12}$ with NH_2 substitution in an ortho position of the pyridine ring. The first CH_3 substituent replaces hydrogen in the ortho position in $C_6N_2H_8$, whereas the second methyl group substitutes the H atom in para position. Benzimidazoles ($C_mN_2H_{2m-8}$: $C_7N_2H_6$, $C_8N_2H_8$, $C_9N_2H_{10}$) are the 10th homologous groups (#10, Figure 2) of magic molecules. Benzimidazole ($C_7N_2H_6$) reacts with active metals with the formation of metal benzimidazolates; its methylated derivative is one of the axial ligands in cobalamin, known as vitamin B_{12}.[54]

C_6NH_5[55] was recently found in the interstellar medium in two isomeric forms, 1-cyanocyclopentadiene and 2-cyanocyclopentadiene. The former is the ground state and has negative Δ^2_{min} (−0.99 eV), which explains its low abundance. Another cyano derivative that was reported as a space molecule is C_7NH_5 (benzonitrile).[56] It has a CN-substituted phenyl ring and is stable according to both Δ^2_{min} and E_{frag} criteria. Benzonitrile is commonly used as a precursor in the manufacturing of thermoresistant materials. Yet another aromatic nitrile derivative is 2-cyanonaphthalene ($C_{11}NH_7$) that has positive values of Δ^2_{min} (1.13 eV) and E_{frag} (3.93 eV). It was detected in space[57] very recently.

Skatole (3-methylindole) is the second isomer (ΔE = 0.13 eV) for compounds with the molecular formula C_9NH_9 and has a near-magic value of Δ^2_{min} (−0.07 eV). It is responsible for the foul odor often associated with feces. In addition to its natural occurrence, skatole is also used in the perfumery and food industry.

3. N-Derivatives of Alkanes. N-derivatives of alkanes include all structures obtained from alkanes, in which H is substituted by −NH, −CN, and $-NH_2$ groups. The 11th homologous series includes simple amines (C_mNH_{2m+3}): CNH_5, C_2NH_7, C_3NH_9, and C_4NH_{11}, possessing high values of Δ^2_{min} (#11 in Figure 2). Methylamine (CNH_5)[58] and ethylamine (C_2NH_7)[59] are present in interstellar medium. They are both widely used as precursors in fine organic synthesis. Cyclopentylamine (C_5NH_{11}), a derivative of cyclopentane, also belongs to amines and has a slightly negative value of Δ^2_{min}. Its isomer, piperidine, is a component of crude oil.[8]

Imines (CNH_3, C_2NH_5, C_3NH_7, C_4NH_9) with the formula C_mNH_{2m+1} form 12th homologous series (#12, Figure 2), almost all of these compounds except CNH_3 (Δ^2_{min} = −0.73 eV) are near-magic (Δ^2_{min} = −0.28, −0.11, and −0.13 eV). Their structures contain a double bond between the C and N atoms, which could be easily protonated or undergo hydrolysis. However, two of them exist in space: ethanimine (C_2NH_5),[60] which is a precursor of alanine (one of the 20 essential amino acids) and propyleneimine (C_3NH_7),[61] found in space very recently.

Simple nitriles (C_3NH_5, C_4NH_7) (#13 in Figure 2) form the 13th homologous series and are cyano-substituted saturated hydrocarbons. Both were registered in the interstellar medium[59,62] and have the widest HOMO−LUMO gap (8.67 and 8.61 eV). A representative of this series, *n*-propyl cyanide (C_3NH_5), is widely used as a solvent and precursor in organic synthesis.

The 14th homologous series is diamines ($C_mN_2H_{2m+4}$: $C_2N_2H_8$, $C_3N_2H_{10}$, $C_4N_2H_{12}$) (#14 in Figure 2); these molecules contain two nitrogen atoms. They are geminal diamines with the formula $C_mN_2H_{2m+4}$, having the maximum number of H atoms.

$C_2N_2H_2$ (Δ^2_{min} = −0.4 eV and E_{frag} = 0.21 eV) is called *E*-cyanomethanimine and may be considered as methane substituted by cyano and imino groups. It was detected in space medium.[63] $C_2N_2H_4$ (aminoacetonitrile) was found in space too.[64] It has a small negative Δ^2_{min} (−0.37 eV) and a negative fragmentation energy (−0.48 eV). As a consequence, this molecule can be formed spontaneously, but over time disintegrates into molecular nitrogen and ethylene.

4. Hydronitrogens. Several N_nH_k molecules have been found in the space: NH,[65] NH_2,[66] NH_3,[3] and N_2.[67] In addition, molecular nitrogen (N_2) and ammonia (NH_3) have dominating concentrations and are the key precursors for the rest of the molecules found in Titan's lower atmosphere.[68] According to our criteria, N_2 and NH_3 are stable by both Δ^2_{min} and E_{frag} (Δ^2_{min}: 3.22 and 4.54 eV, E_{frag}: 9.75 and 4.41 eV), and their values of Δ^2_{min} are among the largest in the compounds studied here. Imidogen radical (NH) and amino radical (NH_2) have negative Δ^2_{min}, but a high fragmentation energy.

Hydrazine (N_2H_4) is a magic representative of this group, but it has not been detected in space so far. Like ammonia, it has positive but lower values of Δ^2_{min} and E_{frag} (0.79 and 1.26 eV), which are related to its higher reactivity. N−N bond in hydrazine is weaker than N−H bonds in ammonia, thus given an excess of hydrogen in the Universe, only ammonia accumulates in planetary atmospheres. N_2H_4 is used as a rocket propellant[69] and serves as a precursor for various compounds used in medicine−synthesis of isoniazid ($C_6N_3H_7O$),[70] used for the treatment of tuberculosis and many other pharmaceutical preparations.[71] Moreover, N_2H_4 serves as a reagent for the synthesis of N_3H (hydrogen azide), a well-known highly explosive compound. N_3H is an almost magic molecule (Δ^2_{min} = −0.33 eV) and has an E_{frag} of 0.96 eV.

To sum up, we applied a novel method for predicting the structures and stability of molecules to the fundamentally important C−N−H system. Stable (or "magic") molecules are those that have lower energy than molecules with closest compositions (i.e., have positive second energy difference, discrete analogue of the second derivative of a function, standard criterion of local minimum of a function). Such molecules can be easily formed, and if their E_{frag} is also positive, they can accumulate in high concentrations. This enables one to analyze large chemical spaces (such as C−N−H) in a clear and insightful way, uncovering major structural classes and homologous series. Magic molecules predicted here correspond well to those found in natural environments: 80% of space molecules, 100% of compounds detected in Titan's

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atmosphere, and 100% of oil components satisfy proposed criteria. Some of the molecules violating these stability criteria still can be made from "criterion-fitting" ones (e.g., C_2NH and C_4NH) when the energy of reaction is negative, thereby providing a key to synthesis strategies. Some of these molecules were precursors to life in early Earth with an anoxic atmosphere. Our very simple approach possesses explicative clarity and great predictive power, enabling one to forecast molecules that are likely to appear in various media. In particular, this could help to direct the ongoing search for interstellar molecules. This work also shows that it is perfectly possible to "rediscover" and rationalize organic chemistry from first principles.

In fact, new molecules are continually being discovered in space. During the final stages of writing this paper, cyanopolyyne C_8NH_3[41] and propylimine (C_3NH_7)[61] were discovered in 2022−2023, and indeed they are magic. Our work, predicting all magic molecules, gives a list of molecules likely to be discovered in space next.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.3c01753.

Atomic coordinates of calculated structures of $C_mN_nH_k$ molecules found in diverse environments (interstellar environments, Titan's atmosphere, crude oil) are given in the XYZ format. Table S1. Data, including stability information, for $C_mN_nH_k$ molecules (n = {1,2}) found in various media (interstellar and circumstellar, oil fractions and Titan's lower atmosphere). Figure S1. Heatmaps interpolating the calculated values of HOMO−LUMO gap in eV for $C_mN_nH_k$ molecules (n = {1,2}) (PDF)

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Notes

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