"Magic" Molecules and a New Look at Chemical Diversity of Hydrocarbons

Sergey V. Lepeshkin,* Vladimir S. Baturin, Anastasia S. Naumova, and Artem R. Oganov

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ABSTRACT: We address the question why among the multitude of imaginable C_nH_m compositions some are easily synthesizable and abundant in nature, while others are not. To shed light on this problem we borrow approaches from nanocluster study, where stability with respect to neighboring compositions is used as a criterion of "magic" (particularly stable) clusters. By merging this criterion with predictions of lowest-energy structures of all C_nH_m molecules in a wide range of compositions ($n \leq 20$, $m \leq 42$) we provide guidelines for predicting the presence or absence of certain hydrocarbon molecules in various environments, their relative abundance and reactivity/inertness. The resulting maps of stability show the increased stability of $C_{2n}H_2$ compounds, polyaromatic hydrocarbons, and diamondoids, which is supported by experimental studies of the interstellar medium, flames, and petroleum fractions. This approach can be applied to any other molecular system, rationalizing the diversity of known compounds and predicting new potentially synthesizable molecules.

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Stability map of C_nH_m molecules
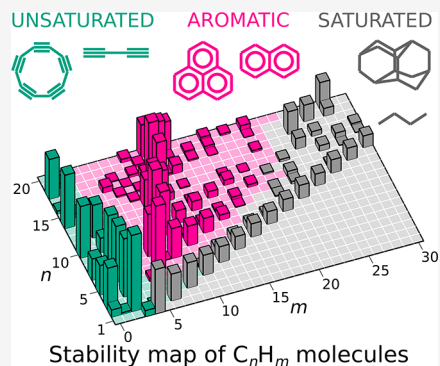
B eing the basis of organic chemistry, hydrocarbons (HC) are perhaps the most fundamentally important molecules, and the most studied one. Made of highly abundant (both on Earth and in the Universe) atoms, connected by covalent C−H and C−C bonds (the latter have a variety of types and can be single, double, triple, or of intermediate character), HCs demonstrate enormous variety in nature and in chemical processes. As a consequence of strong and directional covalent bonds, these molecules have long lifetimes. The importance of HCs extends into many fields, such as astrochemistry, planetary science, studies of combustion, and petrochemistry. For example, highly unsaturated HCs are the likeliest candidates for the carriers of diffuse interstellar spectral bands.[1] Polycyclic aromatic HCs (PAHs), present in fuel-rich hydrocarbon flames,[2] are also thought to be the nucleation agents that promote the growth of the orange-brown aerosol in the atmosphere of Titan.[3] Saturated HCs are the key components of petroleum, hence their obvious practical applications.

An open question is why, among the myriad of possible HC molecules, only some are abundant and others are nearly absent. A similar question was addressed for the crystalline C−H system, where it was found that methane (CH_4) is the only thermodynamically stable compound at normal conditions (under pressure, this changes,[4] but at all pressures, still only saturated hydrocarbons form stable phases). To understand the observed variety of HC molecules, one should consider the nonequilibrium conditions of a given environment (e.g., circumstellar and interstellar space with rare collisions between the molecules, or fast combustion in flames, etc.). Theoretical evaluation of the abundance of a given molecule would involve

the estimations of reaction barriers and lifetimes of molecules in relation to the time scale of the relevant process (from billions of years in case of interstellar space to seconds for flames). For example, such attempts have recently been made to study the mechanisms of formation of benzene,[5] naphthalene,[5,6] and some larger PAHs[7,8] in the interstellar medium and combustion flames. However, this is very challenging, and in practice, only a small part of the relevant compounds can be explored this way.

Another question is the synthesizability of HCs: why are some molecules very easy to synthesize, while others require catalysts and complex precursors? Are there any selection rules, which can indicate whether a given molecule may or may not appear spontaneously in significant quantities? We know empirically which molecules appear in which process (and which do not), while theoretical explanations are absent.

These two problems are related not only to each other, but also to the fundamental questions from other disciplines. The striking parallel is relative abundances of different chemical elements in the Universe and stability of atomic nuclei: some nuclei, known as "magic", are particularly abundant. What are the selection rules, knowing which we could predict magic nuclei? The binding energy of nuclei has a global maximum at
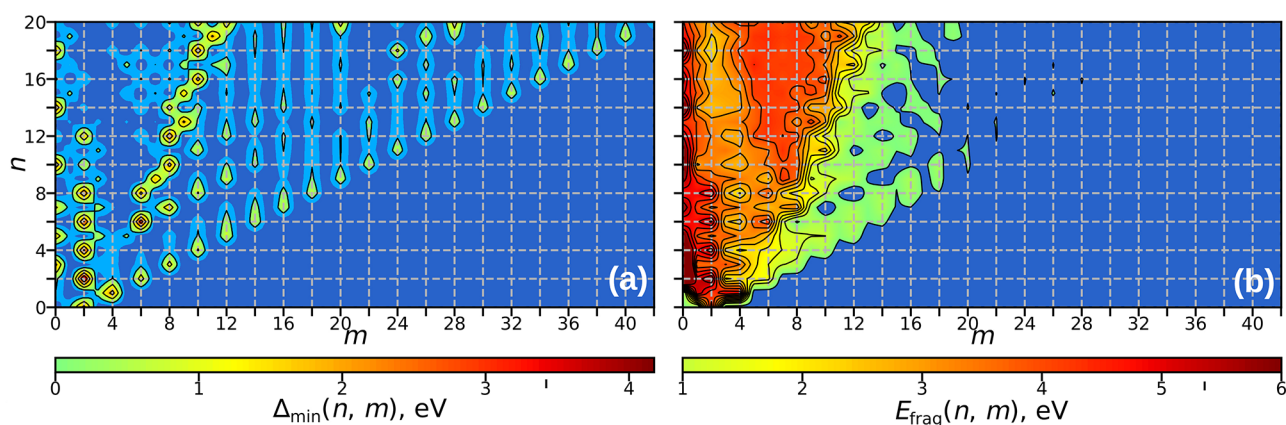
Figure 1. Stability maps of C_nH_m molecules using two criteria: (a) $\Delta_{\min}(n,m)$ and (b) $E_{\mathrm{frag}}(n,m)$ in eV as a function of n and m. Deep blue color denotes unstable compositions. The light blue color in part a indicates the area with $-0.6 < \Delta_{\min} < 0$.

[56]Fe, but this is just one of many magic nuclei. One thing all of them have in common is the corresponding peaks of the binding energy (such as [4]He, ^{12}C, etc.) which shows the importance of local characteristics rather than global ones.

Analogously, nanoparticles of only certain compositions (also called "magic") show particularly high abundance. The binding energy of an ensemble of atoms almost monotonically grows with increasing number of atoms—so, by this criterion only an infinite crystal is stable, and there is no possibility to distinguish magic nanoparticles or molecules. It turns out that instead of looking at global stability, one should analyze local stability with respect to exchanging of one or a few particles. More specifically, if a molecule is more stable than a mixture of molecules of neighboring compositions, we call it magic. Multiple studies have shown that magic nanoparticles often reproduce peaks in experimental mass spectra.[9,10]

Here we use this criterion to predict "magic" hydrocarbon molecules. A prerequisite for applying this criterion is the knowledge of ground-state structures and corresponding energies of the molecules in the entire studied composition range. Despite the availability of vast databases of HC molecules, there are a number of compositions with no information on ground-state structures. In this study, all structures of molecules in the whole compositional space were found using evolutionary global optimization.[11] Knowing all relevant energies, we also computed the minimal fragmentation energies for all ground-state molecules.

The results, as we show, provide a much needed systematic look at hydrocarbons. Usually, textbooks describe hydrocarbons as a series of separate molecules or their classes, i.e., alkanes, alkynes, polyaromatic molecules, etc., without putting all of them in one general context. Our approach provides the holistic picture where all these groups are seen at one glance as distinct regions on the maps of stability, and one can instantly get an understanding of the abundance or ease of synthesis of each molecule and get an intuition about its possible inertness or reactivity.

The ground-state structures of C_nH_m molecules were found in a vast compositional area of $1 \leq n \leq 20$, $0 \leq m \leq 2n + 2$ using our recently developed evolutionary variable-composition global optimization technique for nanoclusters,[11] implemented in the USPEX code.[12,13] The algorithm performs a joint evolutionary search for all molecules in a given range of compositions and takes advantage of exchange of structural information between different compositions. This method has

been applied to various systems[11,14,15] and showed speedup of up to 50 times compared to traditional global optimization done separately for each composition.

To maximize efficiency and accuracy, we first performed the USPEX search in combination with semiempirical PM3 and PM6 approaches (as implemented in the MOPAC code[16]) and used its results as the initial point for another USPEX search coupled with *ab initio* structure relaxations and energy calculations. The latter were done using the projector augmented wave method[17] and PBE exchange-correlation functional[18] as implemented in the VASP code.[19,20] The energies of 20 best structures for each composition were then refined using the GAUSSIAN code with the B3LYP hybrid functional and 6-311+G(d,p) basis sets.[21] The ground-state structures of all calculated molecules are given in Supporting Information.

Knowing energies $E(n,m)$ of the ground-state structures of all C_nH_m molecules, we were able to explore the stability patterns of HCs using two criteria borrowed from nanocluster studies. The first criterion is based on the second-order differences over atoms of each type

$$\Delta_C E(n, m) = E(n + 1, m) + E(n - 1, m) - 2E(n, m),$$

$$\Delta_H E(n, m) = E(n, m + 1) + E(n, m - 1) - 2E(n, m),$$

$$(1)$$

The minimum of the two characterizes the stability of a molecule against transfer of one atom of each type between a pair of identical C_nH_m molecules. This criterion is powerful, because molecules satisfying it are energetically more favorable than neighboring compositions and are thus special. Furthermore, only such molecules can accumulate in significant amounts and not disproportionate during collisions. Since hydrogen exists predominantly in the form of H_2 molecules and the C_nH_m molecules with an odd number of hydrogen atoms are radicals (usually not very stable molecules with open-shell electronic structure), we extended this criterion by including exchange of an H_2 molecule: $\Delta_{H2} E(n,m) = E(n,m + 2) + E(n,m - 2) - 2E(n,m)$. Thus, the final measure of stability is

$$\Delta_{\min}(n, m) = \min\{\Delta_C E(n, m), \Delta_H E(n, m), \Delta_{H2} E(n, m)\}$$

$$(2)$$

HC molecules with positive $\Delta_{min}(n, m)$ will be referred to as "magic".
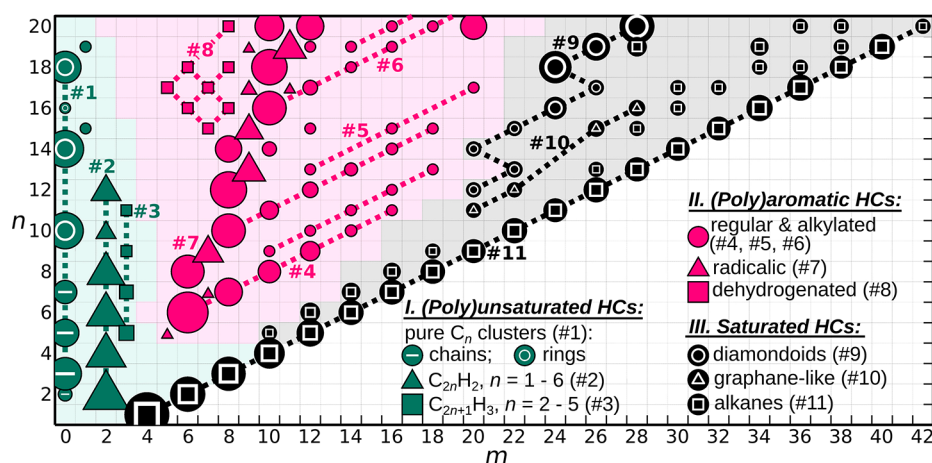
Figure 2. Magic C_nH_m molecules divided into three classes (different colors) and 11 homologous series (different markers). Marker size corresponds to the value of Δ_{min}.

Besides described exchanges there are numerous other reactions, such as exchange of other various fragments, fusion into bigger clusters, *etc*. Of particular importance is the fragmentation of C_nH_m into two fragments C_kH_l and $C_{n-k}H_{m-l}$, the energy of which is

$$E_{frag}(n, m, k, l) = E(k, l) + E(n - k, m - l) - E(n, m) \tag{3}$$

As there are many possible fragmentation channels, we look for the lowest fragmentation energy among all of them: $E_{frag}(n,m) = \min_{k,l} E_{frag}(n,m,k,l)$. As opposed to the "local" criterion (2), this one is more "global".

Panels a and b of Figure 1 show, respectively, the interpolated contour maps of calculated $\Delta_{min}(n,m)$ and $E_{frag}(n,m)$ as a function of n and m. On the first map, one can immediately see as stable the fundamental organic compounds such as methane (CH_4), acetylene (C_2H_2), ethane (C_2H_6), propane (C_3H_8), benzene (C_6H_6), etc. The remarkable variety of stable hydrocarbons is the reason organic chemistry (the chemistry of derivatives of HCs) is so rich— and suitable as the basis of life. Stable compositions form ridges of stability (corresponding to homologous series) or islands of stability. Among the most prominent homologous series, one can notice pure C_n clusters, polyynes $C_{2n}H_2$, PAHs, diamondoids, and alkanes C_nH_{2n+2}.

The map of fragmentation energies $E_{frag}(n,m)$ shows one large area above zero with varying height. Assuming that greater height corresponds to greater stability, the map $E_{frag}(n,m)$ has many similarities with the previous map $\Delta_{min}(n,m)$ reproducing many magic molecules including short C_n chains, C_2H_2 and PAHs. However, it has a distinctive feature, namely an abrupt drop of stability to the right of line $n = 2m - 6$ which represents the border of regular PAHs.

In Figure 2, we schematically show all the magic molecules with focus on the homologous series. Below we discuss these series within the context of their presence in planetary atmospheres, interstellar space, flames and chemical synthesis. We focus on the first criterion of stability since it covers all diversity of HC compounds and use the second criterion as a complementary one. For convenience of description, we have conventionally divided the resulting compounds into three classes: polyunsaturated HCs (compounds with multiple double or triple bonds), PAHs, and HCs with saturated C– C bonds only (alkanes, cycloalkanes, graphanes, diamondoids).

1. *(Poly)unsaturated HCs* of magic compositions are shown in Figure 3. The first series is the pure carbon clusters (#1,
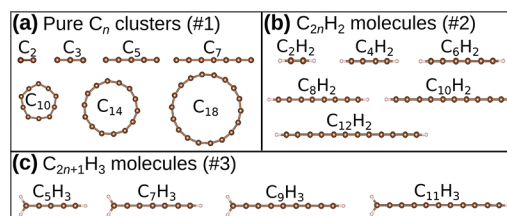
Figure 3. Structures of magic (poly)unsaturated HCs.

Figure 3a) including C_2, C_3, C_5, C_7, C_{10}, C_{14}, and C_{18}, which agrees with previous studies.[22] C_3, C_5, and C_7 are linear chains and C_{10}, C_{14}, and C_{18} are rings. The smallest of them, namely C_2, C_3, and C_5, were indeed found in the interstellar media[23−25]

The second series of magic compounds is polyynes with the formula $C_{2n}H_2$ (#2, Figure 3b). Their degrees of stability Δ_{min} are among the highest of all HC compounds. Yet these values decrease with n, falling below zero for $n > 6$. The second criterion also shows that molecules $C_{2n}H_2$ ($n = 1-4$) are of the highest stability. There is abundant evidence for the presence of these compounds in different environments. C_2H_2, C_4H_2 and C_6H_2 chains were detected in the circumstellar medium of the proto−planetary nebula CRL 618.[1] $C_{2n}H_2$ molecules with $n = 1−5$ were detected in planetary atmospheres, interstellar space and fuel-rich flames[26,27] and those with n up to 8 were detected in laser ablation experiments on graphite, coal, and C_{60} particles suspended in solutions.[28] Diacetylene C_4H_2 also was found in Titan's atmosphere.[29] $C_{2n}H_2$ molecules with n up to 13 were also observed in rare gas matrices by direct absorption spectra.[30−32] The simplest polyynes are proposed to be common intermediates in HC combustion. They play an important role in synthesis of large carbonaceous molecules such as PAHs, fullerenes, and constitute a large part of soot.

We single out $C_{2n+1}H_3$ molecules ($n = 2-5$) as the third homologous series (#3, Figure 3c). These have an odd number of electrons and therefore are magnetic and classified as radicals, and known to play an important role in interstellar, combustion and plasma chemistry. They are dominant products in acetylene, benzene, and diacetylene discharges, and are also produced in fuel-rich flames.[26]

2. *(Poly)aromatic HCs* can be divided into three main groups: regular, radicalic, and dehydrogenated PAHs. The molecules with an even number of hydrogen atoms will be referred to as "regular", while the ones with an odd number—as "radicalic". Typical structures for each group are shown in Figure 4. Regular PAHs include benzene (C_6H_6), naphthalene
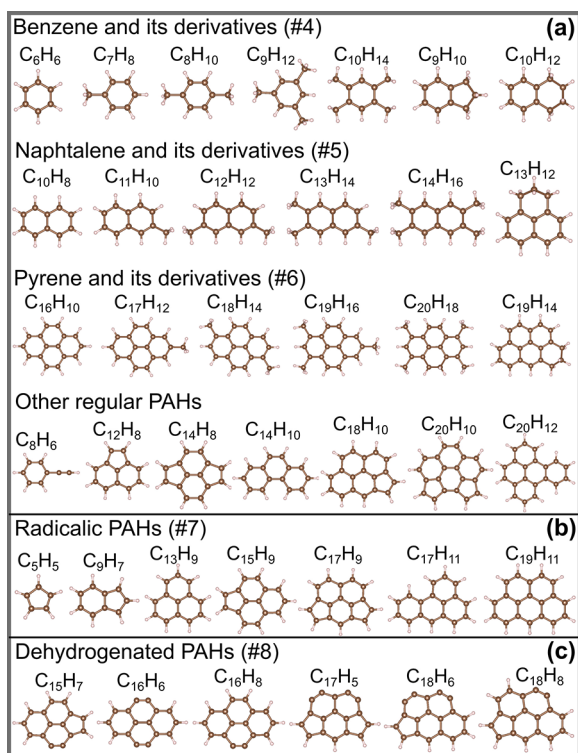

Figure 4. Structures of magic (poly)aromatic HCs.

($C_{10}H_8$), acenaphthylene ($C_{12}H_8$), pyracyclene ($C_{14}H_8$), phenanthrene ($C_{14}H_{10}$), and larger PAHs (Figure 4a). They all possess large Δ_{min}. Many of these compounds were observed in the interstellar and circumstellar media, as well as planetary atmospheres (e.g., Titan): C_6H_6, $C_{10}H_8$, $C_{12}H_8$, $C_{14}H_{10}$, and larger molecules.[33,34]

It is worth mentioning that many PAHs appear as natural minerals such as carpathite,[35] kratochvilite,[36] or ravatite,[37] which are crystalline forms of coronene ($C_{24}H_{12}$), fluorene ($C_{13}H_{10}$), and anthracene ($C_{14}H_{10}$), respectively. Some minerals are mixtures: curtisite is made of several PAH compounds,[38] including dibenzofluorene, picene ($C_{22}H_{14}$), and chrysene ($C_{18}H_{12}$), while idrialite[39] is mostly composed of tribenzofluorenes. Their occurrence in nature had been explained by burial of PAHs until they reached a temperature where pyrolysis took place, followed by hydrothermal transport toward the surface, where the composition of precipitating minerals depends on.[40]

Functionalized PAHs, where hydrogen atoms are substituted, e.g., by methyl groups, are also present on the map, although with lower degrees of stability Δ_{min}. On our map these compounds are represented by three series: derivatives of benzene (#4), naphthalene (#5) and phenanthrene (#6). In each of them, the number and size of substitutions consequently increases. However, at some extent of substitution atoms, they become less stable than the diamondoids of the same compositions.

Another series of magic compounds is radicalic PAHs, such as C_5H_5, C_9H_7, $C_{11}H_7$, $C_{13}H_9$, and larger molecules (#7, Figure 4b). Despite the presence of an unpaired electron, their stability Δ_{min} is comparable to that of regular PAHs. This is explained by atomic closed-shell structure and high single electron delocalization among the aromatic system. The observations show the presence of such molecules in the planetary atmospheres; in particular, C_9H_7 was found on Titan.[34]

Finally, we note dehydrogenated PAHs, which are formed from regular PAHs by removal of an even number of hydrogen atoms (#8, Figure 4c). The degree of stability Δ_{min} of these compounds is just above 0, which indicates low probability of their detection in different environments. And indeed, these compounds were not observed in space, but can be intermediates during chemical synthesis. For example, $C_{16}H_8$ was observed in mass-spectra of the products of pyrolysis of benzene.[41]

3. *Saturated HCs* with magical compositions are shown in Figure 5. The ninth series of magic compounds is diamond-
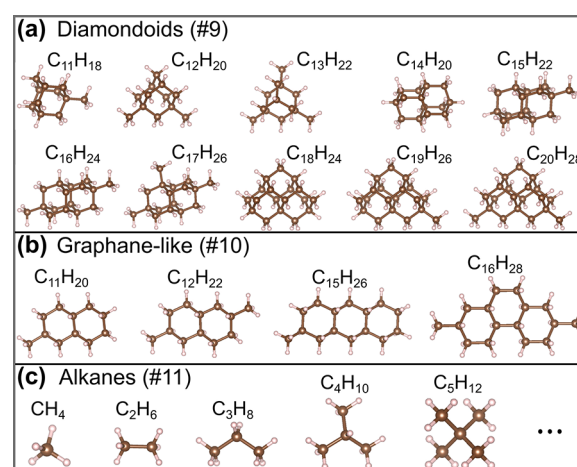

Figure 5. Structures of magic saturated HCs.

oids—cage hydrocarbon molecules, carbon backbones of which are fragments of the diamond structure (#9, Figure 5a). The simplest diamondoid is adamantane with formula $C_{10}H_{16}$, but its Δ_{min} is slightly negative. Larger diamondoids become more stable and appear on the stability map. Diamondoids were found in oil and gas condensates[42] and their amount reflects the extent of the natural oil cracking.[43] Yet another class of magic saturated hydrocarbons is graphane-like structures, the carbon backbone of which corresponds to a layer of diamond structure (#10, Figure 5b). Unlike diamondoids with cage-like carbon backbone, graphane-like hydrocarbons have puckered 2D-carbon backbone.

The final and the simplest group of saturated HCs is alkanes with formula C_nH_{2n+2} (#11, Figure 5c). Alkanes can be found in most environments containing HCs and are all present on the stability map $\Delta_{min}(n,m)$. It can be noted that their degree of stability Δ_{min} decreases as the number of carbon atoms increases, which is in line with expectations.

The provided analysis showed that magic molecules are indeed present in various media. At the same time, our maps carry more information than whether a cluster is magic or not: the values Δ_{min} and E_{frag} can be seen as quantitative measures of stability and abundance. This makes sense, e.g., for the

interstellar media, where collisions are rare and even compounds with Δ_{min} slightly below zero can be found. To date, 27 HC compounds of 24 compositions have been detected there (plus fullerene C_{60}, which is outside the considered composition area).[44] Nine species have remarkably high values of both Δ_{min} and E_{frag} (C_3, C_5, H_2, C_2H_2, C_4H_2, C_6H_2, CH_3, CH_4, C_6H_6), 13 compounds have near-zero or slightly negative Δ_{min}, but high values of E_{frag} (C_2, C_2H_4, C_9H_8, C_nH radicals with $n = 2-8$ and $C_{2n+1}H_4$ with $n = 1-3$), and only three compounds have a value of Δ_{min} significantly below zero (CH, CH_2, C_3H_2). Thus, if we modify our criterion to $\Delta_{min} > -0.6$ eV (region with $-0.6 < \Delta_{min} < 0$ is shown in light-blue in Figure 1a) and $E_{frag} > 2$ eV, we immediately obtain 20 of 24 ($\sim$83%) compositions of HC molecules in the interstellar media, which proves a great accuracy of our approach.

One can also compare our predictions with the abundances of HC molecules found in crude oil. The main components are alkanes (paraffins), cycloalkanes (naphthenes), and aromatics with average contents of 30, 49 and 15%, respectively.[45] Note that merely from combinatorial reasons, the number of possible chemical compositions of cycloalkanes is much greater than that of alkanes, so the concentrations of individual cycloalkanes are low compared to alkanes, while the total amount is comparable. Our Δ_{min} stability map predicts remarkable stability for alkanes and near-zero stability for cycloalkanes, which is consistent with the prediction.

Finally, our stability maps can rationalize data on chemical synthesis of HC molecules. In general, one can suggest the following tendency: molecules with a positive Δ_{min} can be easily obtained in the pure C−H system and will form spontaneously and in significant quantities; molecules with Δ_{min} near 0 can be obtained from other hydrocarbons, but using catalysts. Synthesis of molecules with negative Δ_{min} requires either precursors or substances with other types of atoms, i.e., beyond the pure C−H system. The predictive power of the maps goes beyond just indicating the easily synthesizable and stable molecules. It is instructive to look at the seeming exceptions—the well-known molecules, which do not satisfy the stability criterion of eq 2. Let us consider three famous molecules of this kind. Cyclopropane C_3H_6 is understandably not magic, because of strained bonds (C−C−C angle of 60°, very far from the ideal angle of 109.5° for sp^3 hybridization). Indeed, this molecule is produced via a brominated precursor cyclized using sodium. Butadiene C_4H_6 is also not magic, and indeed it is synthesized from alcohols (i.e., in the C−H−O system) or using catalysts. Its nonmagicity explains its high reactivity and propensity for polymerization, used for industrial production of rubber. Cyclobutadiene C_4H_4, a textbook illustration of the Jahn−Teller effect in organic molecules, is synthesized from complex precursors and has a strong tendency to dimerization and for that reason has only been isolated as single molecules in inert matrices.

Concluding, we found the ground-state structures of C_nH_m molecules in an unprecedentedly wide compositional area ($1 \leq n \leq 20$, $0 \leq m \leq 2n + 2$) and applied the approach from the nanocluster study, where the stability of each molecule is evaluated with respect to neighboring compositions. This allowed us to determine magic compositions, which are expected to form spontaneously, without catalysts or complex precursors, and have indeed been found to form in various natural systems (interstellar and circumstellar media, planetary atmospheres, flames, petroleum), as well as in experiments.

These results allowed us to show the wide diversity of HC molecules. We showed how homologous series, so essential for the description of HC chemistry, naturally emerge from our stability maps as ridges and islands of stability. This approach can be applied to any molecular or cluster system, as well as clusters on substrate, revealing a comprehensive picture of its chemistry in one shot.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.2c02098.

Coordinates of all ground-state structures of C_nH_m molecules ($1 \leq n \leq 20$, $0 \leq m \leq 2n + 2$) calculated at the ab initio level (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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