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Journal

Angewandte Chemie International Edition, 59(28)

ISSN

1433-7851

Authors

Zhao, Long

Kaiser, Ralf I

Lu, Wenchao

et al.

Publication Date

2020-07-06

DOI

10.1002/anie.202003402

Peer reviewed



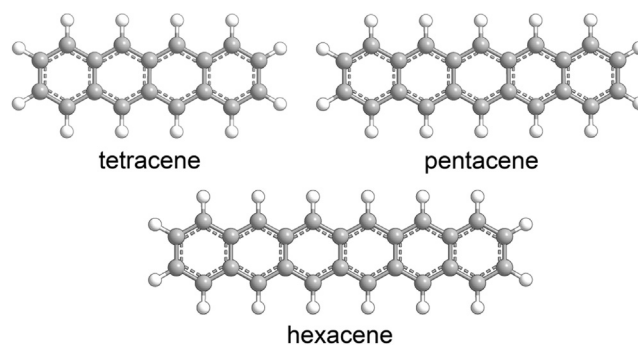
A Free-Radical Prompted Barrierless Gas-Phase Synthesis of Pentacene

Long Zhao, Ralf I. Kaiser,* Wenchao Lu, Musahid Ahmed,* Mikhail M. Evseev, Eugene K. Bashkirov, Valeriy N. Azyazov, Christina Tönshoff, Florian Reicherter, Holger F. Bettinger,* and Alexander M. Mebel*

Abstract: A representative, low-temperature gas-phase reaction mechanism synthesizing polyacenes via ring annulation exemplified by the formation of pentacene ($C_{22}H_{14}$) along with its benzo[a]tetracene isomer ($C_{22}H_{14}$) is unraveled by probing the elementary reaction of the 2-tetracenyl radical ($C_{18}H_{11}^{\cdot}$) with vinylacetylene (C_4H_4). The pathway to pentacene—a prototype polyacene and a fundamental molecular building block in graphenes, fullerenes, and carbon nanotubes—is facilitated by a barrierless, vinylacetylene mediated gas-phase process thus disputing conventional hypotheses that synthesis of polycyclic aromatic hydrocarbons (PAHs) solely proceeds at elevated temperatures. This low-temperature pathway can launch isomer-selective routes to aromatic structures through submerged reaction barriers, resonantly stabilized free-radical intermediates, and methodical ring annulation in deep space eventually changing our perception about the chemistry of carbon in our universe.

Since the very first isolation of tetracene ($C_{18}H_{12}$) and pentacene ($C_{22}H_{14}$) respectively by Gabriel and Leupold (1898) and Clar and John (1929, 1930)^[1] more than a century ago, acenes—polycyclic aromatic hydrocarbons (PAHs) with the molecular formula $C_{4n+2}H_{2n+4}$ ($n \geq 4$) formally grown by linear fusion of benzene molecules^[2] (Scheme 1)—have attracted extensive attention from the physical chemistry, organic chemistry, material science, and astrochemistry communities. This interest is based on their exceptional optoelectronic properties—often in combination with Buckminsterfullerene (C_{60})—as organic semiconductors^[3] and

organic field effect transistors (OFETs).^[4] Acenes also play a fundamental role as molecular building blocks in nanotubes,^[5] graphenes,^[6] nanoflakes,^[7] and fullerenes (C_{70}) (Scheme 2)^[8] and have been suggested as potential carriers of (some of) the diffuse interstellar bands (DIBs)^[9]—discrete absorption features overlaid on the interstellar extinction curve from the blue part of the visible (400 nm) to the near-infrared (1.2 μm).^[10] Structurally, the 22 π -aromatic pentacene ($C_{22}H_{14}$) represents a linear (planar) acene with tetracene ($C_{18}H_{12}$) and hexacene ($C_{26}H_{16}$) defining the previous and next member in the homologous series, respectively. Although unsubstituted acenes hold a D_{2h} point group, substitution by phenyl groups in pentacene distorts the



Scheme 1. Molecular structures of the three simplest acenes: tetracene ($C_{18}H_{12}$), pentacene ($C_{22}H_{14}$), and hexacene ($C_{26}H_{16}$). Carbon atoms gray and hydrogen atoms white.

[*] L. Zhao, R. I. Kaiser
Department of Chemistry
University of Hawaii at Manoa
Honolulu, HI 96822 (USA)
E-mail: ralfk@hawaii.edu

W. Lu, M. Ahmed
Chemical Sciences Division
Lawrence Berkeley National Laboratory
Berkeley, CA 94720 (USA)
E-mail: MAhmed@lbl.gov

M. M. Evseev, E. K. Bashkirov
Samara National Research University
Samara 443086 (Russian Federation)

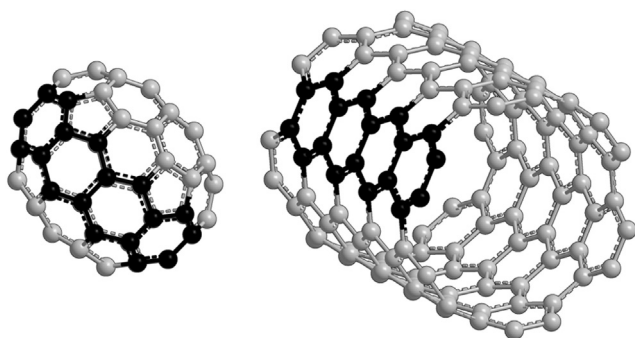
V. N. Azyazov
Lebedev Physical Institute
Samara 443011 (Russian Federation)
and
Samara National Research University
Samara 443086 (Russian Federation)

C. Tönshoff, F. Reicherter, H. F. Bettinger
Institute of Organic Chemistry
University of Tübingen
Auf der Morgenstelle 18, 72076 Tübingen (Germany)
E-mail: holger.bettinger@uni-tuebingen.de

A. M. Mebel
Department of Chemistry and Biochemistry
Florida International University
Miami, FL 33199 (USA)
E-mail: mebela@fiu.edu

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
<https://doi.org/10.1002/anie.202003402>.

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Scheme 2. Acenes as fundamental building blocks in fullerenes and carbon nanotubes; the acene moiety is highlighted in black.

acene moiety out of plane resulting in right- and left-handed enantiomers with end-to-end twists of 144° .^[11] Considering the highly reactive 6 and 13 positions of pentacene due to π -electron localization, the aromatic character of pentacene is quite distinct from PAHs such as naphthalene ($C_{10}H_8$). This is evident from the facile oxidation of pentacene at the 6 and 13 positions to pentacene quinone^{[1b],[12]} and a tautomeric equilibrium between 6-methylpentacene and 6-methylene-6,13-dihydropentacene favoring the methylene species.^[13]

There are a number of ways to synthesize acenes. Classical approaches involve the reduction of acenequinones, the deoxygenation of epoxyacenes, and the dehydrogenation of hydroacenes.^[14] More recent techniques are the photo bisdecarbonylation of bridged α -diketones (Strating–Zwanenburg reaction)^[15] and the photochemical or thermal extrusion of carbon monoxide, a retro-cheletropic reaction.^[16] The latter two approaches were exploited successfully for the generation of the largest acenes under matrix isolation conditions and in ultrahigh vacuum on noble metal surfaces: heptacene ($n=7$), octacene ($n=8$), nonacene ($n=9$), and undecacene ($n=11$).^[17,18] Based on the absorption spectra, an optical gap of 1.2 eV was extrapolated for the infinitely long polyacene.^[17c] Nonacene ($n=9$), decacene ($n=10$), undecacene ($n=11$), and dodecacene ($n=12$) were prepared in situ on gold surfaces using α -diketone, hydroacene, and epoxyacene precursors.^[18] The HOMO–LUMO gap of undecacene was determined to be only 1.2 eV and increases for dodecacene to 1.4 eV.^[18] However, despite extraordinary progress on the synthesis and characterization of higher acenes, molecular mass growth processes leading to these aromatic molecules at extreme temperatures of 10 K as present in molecular clouds have not been reported yet. A fundamental understanding of these processes is critical not only to constrain the formation of a key class of aromatic compounds—acenes—in deep space (after all, if acenes contribute to the DIBS carriers, they have to be synthesized in the interstellar medium), but also to elucidate non-traditional, low-temperature reaction mechanisms to precursors to carbonaceous nanostructures in interstellar environments eventually bringing us closer to an understanding of the carbon chemistry in our Universe.

Herein, we report on a pathway to synthesize polyacenes through a targeted, vinylacetylene prompted gas-phase chemistry via ring annulation involving bimolecular reactions with aryl radicals. In distinction to aforementioned routes

pursuing gas-phase pyrolysis of labile precursors,^[19] preparative high-temperature solution chemistry,^[20] and matrix isolation,^[21] the novel gas-phase synthesis involves a de-facto barrierless reaction via molecular mass growth from the bottom-up via ring addition involving free-radical reaction intermediates. Exploiting pentacene as a prototype, we expose the previously unknown gas-phase chemistry forming pentacene ($C_{22}H_{14}$; 278 amu) along with atomic hydrogen (1 amu) through the elementary reaction of the 2-tetracenyl radical ($C_{18}H_{11}$; 227 amu) with vinylacetylene (C_4H_4 ; 52 amu). Tetracene has been proposed to exist in the interstellar medium (ISM);^[9] the 2-tetracenyl radical can be generated from tetracene via photolysis by the internal ultraviolet field existing even deep inside molecular clouds. Laboratory studies have shown that vinylacetylene can be synthesized in deep space via the barrier-less gas-phase reaction of ethylene (C_2H_4) with the ethynyl radical (C_2H).^[22] Engaging a combination of laboratory experiments and ab initio electronic structure calculations, this proof-of-concept study reveals a benchmark of an unconventional, barrierless reaction through resonance-stabilized free radical (RSFR) intermediates ($C_{22}H_{15}^*$) leading to an efficient gas-phase synthesis of pentacene. This route represents a facile, representative mechanism to systematically build up more complex polyacenes such as hexacene and heptacene through successive ring annulation—one ring at a time—involving bimolecular gas-phase reactions of an aryl radical with vinylacetylene. The extracted reaction mechanism also allows a selective design of substituted acenes by replacing hydrogen atoms in the aryl and/or vinylacetylene reactant(s) by organic groups thus connecting to substituted acenes, whose classical synthetic chemistry has been proven challenging. These processes operate even at ultralow interstellar temperatures as low as 10 K hence providing an unconventional synthetic route to potential carriers of DIBs: polyacenes. Briefly, a chemical microreactor was utilized to synthesize pentacene through the gas-phase reaction of the 2-tetracenyl radical ($C_{18}H_{11}^*$) with vinylacetylene (C_4H_4). The nascent reaction products were sampled in a molecular beam isomer-specifically via fragment-free photoionization of the neutral products exploiting tunable vacuum ultraviolet (VUV) light followed by detection of the ionized molecules in a reflectron time-of-flight mass spectrometer (ReTOFMS; see Supporting Information).

A representative mass spectrum recorded at a photoionization energy of 9.50 eV is displayed in Figure 1 for the reaction of the 2-tetracenyl radical ($C_{18}H_{11}^*$; 227 amu) formed via flash pyrolysis of 2-bromotetracene with vinylacetylene (C_4H_4 ; 52 amu). Control experiments were also carried out by replacing the vinylacetylene reactant with non-reactive helium carrier gas (Figure 1). A comparison of both data sets reveals compelling evidence on the formation of a molecule with the molecular formula $C_{22}H_{14}$ (278 amu) in the 2-tetracenyl–vinylacetylene system (Figure 1 b); this signal is absent in the control experiment (Figure 1 a). Considering the molecular weight of the reactant molecules and the products, it is evident that the $C_{22}H_{14}$ isomer(s) together with the hydrogen atom are formed via the reaction of the 2-tetracenyl radical with vinylacetylene. Note that signal at m/z 252

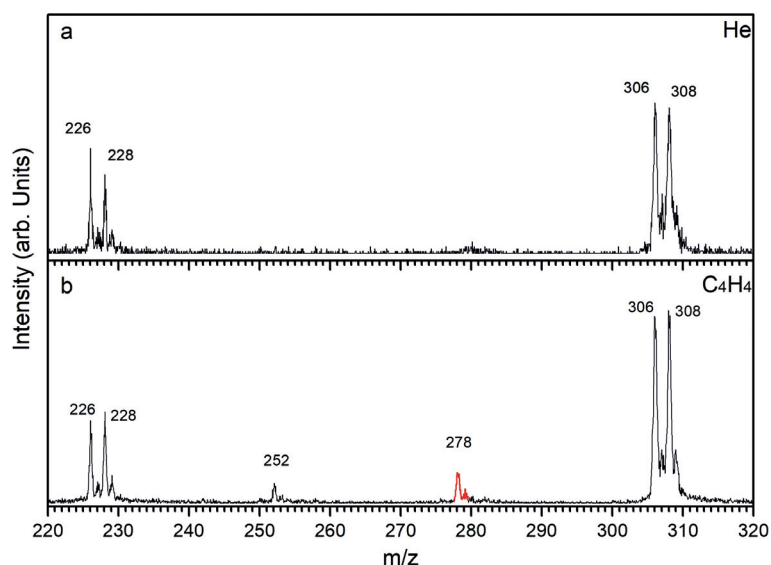


Figure 1. Photoionization mass spectra recorded at a photoionization energy of 9.0 eV. a) 2-tetracenyl ($C_{18}H_{11}$)—helium (He) system; b) 2-tetracenyl ($C_{18}H_{11}$)—vinylacetylene (C_4H_4) system. The mass peaks of the newly formed $C_{22}H_{14}$ (m/z 278) species along with the ^{13}C -substituted counterpart (m/z 279) are highlighted in red.

($C_{20}H_{12}$) is likely linked to 2-ethynyltetracene formed via the reaction of the 2-tetracenyl radical ($C_{18}H_{11}$; 227 amu) with acetylene (C_2H_2 ; 26 amu; Supporting Information). Ion counts at mass-to-charge ratios (m/z) from 306 to 309 ($C_{18}H_{11}^{79}Br^+$, $^{13}CC_{17}H_{11}^{79}Br^+$, $C_{18}H_{11}^{81}Br^+$, $^{13}CC_{17}H_{11}^{79}Br^+$) and from 226 to 229 ($C_{18}H_{10}$, $^{13}CC_{17}H_{10}/C_{18}H_{11}$, $C_{18}H_{12}$, $^{13}CC_{17}H_{10}$) are evident in the 2-tetracenyl—vinylacetylene and helium-vinylacetylene systems; this finding suggests that these molecules are not connected to the gas-phase reaction of the 2-tetracenyl radical with vinylacetylene. Here, ion counts at m/z 306–309 are connected to the non-pyrolyzed 2-bromotetracene precursor, while signals at m/z 226 and 227

are associated with $C_{18}H_{10}$ and ^{13}C - $C_{17}H_{10}$ formed via hydrogen abstraction from the 2-tetracenyl radical and its ^{13}C -substituted counterpart. Finally, ion counts at m/z 228 and 229 are likely traced to tetracene and ^{13}C -tetracene, respectively, and/or originate from dissociative photoionization of the precursor (Supporting Information).

With the detection of hydrocarbon molecules holding the molecular formula $C_{22}H_{14}$ formed through reactive collisions of the 2-tetracenyl radical with vinylacetylene, we aim to assign the structural isomer(s) synthesized in this reaction. This requires an in-depth analysis of the corresponding photoionization efficiency (PIE) curve, which displays the intensity of the ion at m/z of 278 ($C_{22}H_{14}^+$) as a function of the photon energy from 6.60 eV to 9.00 eV (Figure 2). This graph could be reproduced through a linear combination of two distinct reference PIE curves of discrete $C_{22}H_{14}$ isomers: pentacene (green) and benzo[*a*]tetracene (blue; Figure 2). The experimental and reference PIE curves for pentacene show an onset of 6.65 ± 0.05 eV, which agrees nicely with the literature value of the adiabatic ionization energy of 6.61 eV.^[23] The addition of the reference PIE curve of benzo[*a*]tetracene significantly improves the fits from 7.20 to 9.0 eV and accounts for $11 \pm 5\%$ in the ion counts at 9.0 eV. Fitting the experimental data only with pentacene does not reproduce the curve. It is important to highlight that both reference curves were recorded in an identical experimental setup as the 2-tetracenyl—vinylacetylene reaction (Supporting Information). After scaling, the PIE curve at m/z 279 nicely matches the PIE curve of m/z 278; therefore, signal at m/z 279 is associated with ^{13}C -pentacene and ^{13}C -benzo[*a*]tetracene. We would like to stress that absolute photoionization cross sections of these isomers are unknown, and

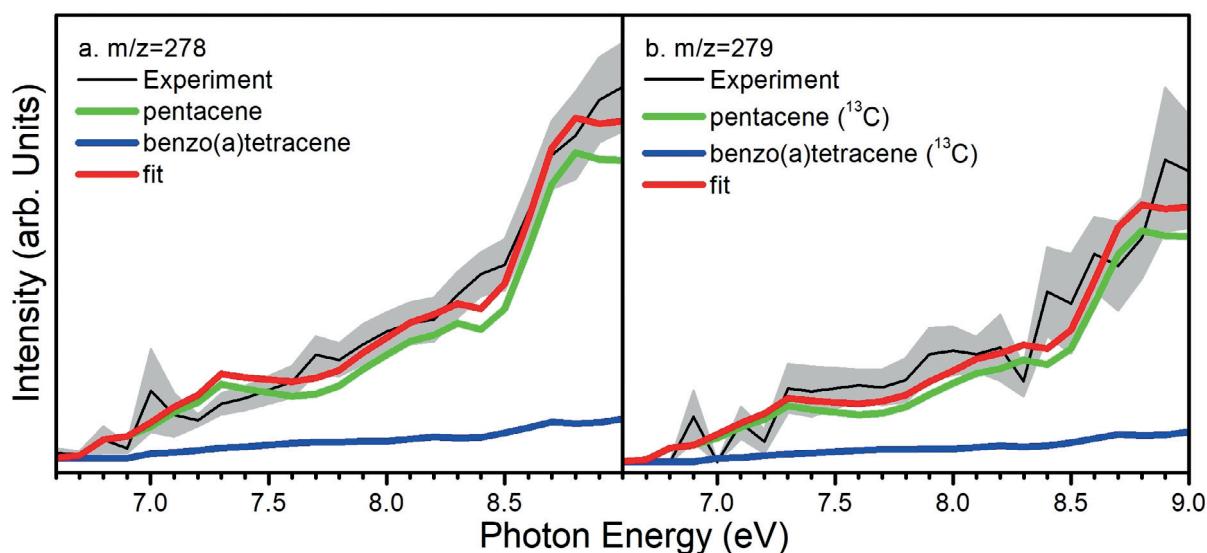


Figure 2. Photoionization efficiency (PIE) curves for m/z 278 and 279. Black: experimentally derived PIE curves with the error area presented in gray; green: pentacene reference PIE curve; blue: benzo[*a*]tetracene PIE curve; red: overall fit. The overall error bars consist of two parts: $\pm 10\%$ based on the accuracy of the photodiode and a 1σ error of the PIE curve averaged over the individual scans.

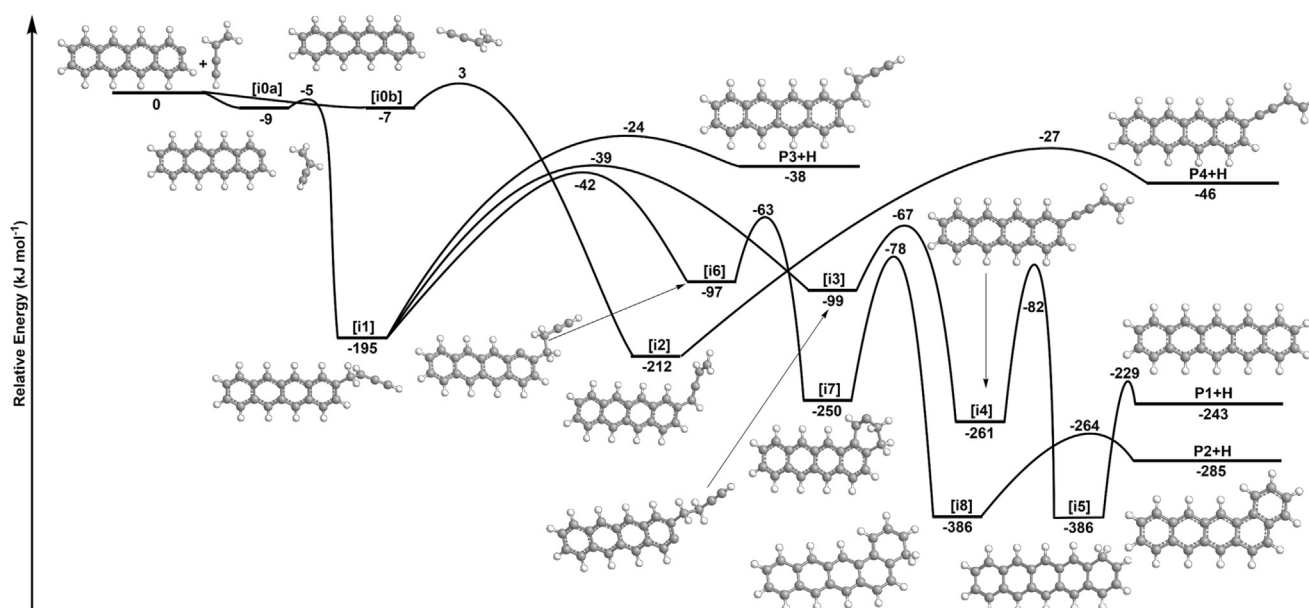


Figure 3. Potential energy surface (PES) for the 2-tetracenyl ($C_{18}H_{11}\cdot$) reaction with vinylacetylene (C_4H_4). See text for details. This PES was calculated at the G3(MP2,CC)//B3LYP/6-311G(d,p) level of theory leading to pentacene and its isomer benzo[*a*]tetracene. The relative energies are given in kJ mol^{-1} .

absolute branching ratios cannot be provided. However, the goal of the present investigation is to provide explicit evidence on the synthesis of pentacene within the 2-tetracenyl–vinylacetylene system.

With the explicit experimental evidence on the detection of pentacene ($C_{22}H_{14}$, **P1**) along with its isomer benzo[*a*]tetracene (**P2**) formed via the reaction of 2-tetracenyl with vinylacetylene in the gas phase, it is our goal to untangle the underlying reaction mechanisms. In case of complex systems, it is very beneficial to merge the experimental findings with electronic structure calculations to explore the synthetic routes (Figure 3). Our computations at the G3(MP2,CC)//B3LYP/6-311G(d,p) level of theory reveal that the 2-tetracenyl radical approaches the vinylacetylene reactant barrierlessly leading to the formation of two possible van-der-Waals complex [i0a] and [i0b] which are stabilized by 9 and 7 kJ mol^{-1} with respect to the separated reactants. The 2-tetracenyl radical adds to vinylacetylene at the terminal carbon atoms of the vinyl and ethynyl moieties yielding the intermediates [i1] and [i2], respectively through barriers of 4 and 10 kJ mol^{-1} relative to [i0a] and [i0b], respectively. It is important to highlight that the barrier connecting the van-der-Waals complex [i0a] to the resonantly stabilized free radical (RSFR) intermediate [i1] is below the energy of the separated reactants. In this sense, a barrier to addition exists, but the latter resides lower in energy than the reactants and hence is called a submerged barrier.^[24] Intermediate [i1] is central to the formation of the pentacene (**P1**) and benzo[*a*]tetracene (**P2**) products; these isomers are synthesized via the reaction sequences [i1] → [i3] → [i4] → [i5] → **P1** and [i1] → [i6] → [i7] → [i8] → **P2** involving a hydrogen atom migration from an *ortho* carbon in the attacked ring of tetracenyl to β -carbon in the side chain, cyclization, another hydrogen atom migration in the newly formed six-member ring (from the methylene

moiety to the neighboring bare carbon atom), and atomic hydrogen elimination accompanied by aromatization and ring annulation. Two thermodynamically less favorable isomers, (*E*)-2-(but-1-en-3-yn-1-yl)tetracene (**P3**) and 2-(but-3-en-1-yn-1-yl)tetracene (**P4**), were not detected in our experiment. In principle, these molecules can be accessed via a hydrogen atom loss from intermediates [i1] and [i2], respectively. Considering (*E*)-2-(but-1-en-3-yn-1-yl)tetracene (**P3**), the barrier of [i1] → **P3** plus hydrogen is higher than the competing isomerization [i1] → [i3] and [i1] → [i6]; therefore, isomerization and eventual formation of pentacene (**P1**) and benzo[*a*]tetracene (**P2**) is preferred compared to decomposition to (*E*)-2-(but-1-en-3-yn-1-yl)tetracene (**P3**), at least at low temperatures when the entropy factor does not play a significant role. For 2-(but-3-en-1-yn-1-yl)tetracene (**P4**), the van-der-Waals complex [i0b] has to isomerize via a higher barrier to [i2] making the addition to the vinyl moiety more likely.

In conclusion, our study identified pentacene (**P1**) and benzo[*a*]tetracene (**P2**) as key products of the reaction of the 2-tetracenyl radical with vinylacetylene. The reaction was found to be barrierless and exoergic with all transition states involved located below the energy of the separated reactants. Considering these critical features along with the submerged barrier to reaction, the bimolecular reactions of the 2-tetracenyl radical with vinylacetylene reveals a facile pathway to synthesize complex PAHs—acenes—in low-temperature interstellar conditions (10 K) as present in cold molecular clouds, such as TMC-1 and OMC-1. Consequently, the hydrogen-abstraction-vinylacetylene-addition (HAVA) mechanism represents a unique low-temperature pathway propelling molecular mass growth processes of aromatic systems via barrierless, successive ring annulation involving

elementary reactions of aryl radical with vinylacetylene as a molecular building block.

Acknowledgements

This work was supported by the US Department of Energy, Basic Energy Sciences DE-FG02-03ER15411 (experimental studies) DE-FG02-04ER15570 (computational studies) to the University of Hawaii and Florida International University, respectively. M.A. is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231, through the Gas Phase Chemical Physics program of the Chemical Sciences Division. The ALS is supported under the same contract. Ab initio calculations at Samara University were supported by the Ministry of Science and Higher Education of the Russian Federation under Grant No. 14.Y26.31.0020. H.F.B.'s group was supported by the Fonds der chemischen Industrie and Deutsche Forschungsgemeinschaft.

Conflict of interest

The authors declare no conflict of interest.

Keywords: gas-phase chemistry · hydrogen abstraction / vinylacetylene addition (HAVA) · interstellar medium · mass spectrometry · polycyclic aromatic hydrocarbons (PAHs)

- [1] a) S. Gabriel, E. Leupold, *Ber. Dtsch. Chem. Ges.* **1898**, 31, 1272; b) E. Clar, F. John, *Ber. Dtsch. Chem. Ges.* **1929**, 62B, 3021; c) E. Clar, F. John, *Ber. Dtsch. Chem. Ges.* **1930**, 63B, 2967; d) I. Ionita, A. Bercea, S. Brajnicov, A. Matei, V. Ion, V. Marascu, B. Mitu, C. Constantinescu, *Appl. Surf. Sci.* **2019**, 480, 212.
- [2] E. Clar, *Ber. Dtsch. Chem. Ges. B* **1939**, 72B, 2137.
- [3] a) R. Bhatia, D. Wadhawa, G. Gurtu, J. Gaur, D. Gupta, *J. Saudi Chem. Soc.* **2019**, 23, 925; b) Z. He, Z. Zhang, S. Bi, *J. Mater. Sci. Mater. Electron.* **2019**, 30, 20899.
- [4] R. R. Tykwinski, *Acc. Chem. Res.* **2019**, 52, 2056.
- [5] K. Kuroda, K. Yazaki, Y. Tanaka, M. Akita, H. Sakai, T. Hasobe, N. V. Tkachenko, M. Yoshizawa, *Angew. Chem. Int. Ed.* **2019**, 58, 1115; *Angew. Chem.* **2019**, 131, 1127.
- [6] M. Altarawneh, I. Oluwoye, B. Z. Dlugogorski, *Combust. Flame* **2020**, 212, 279.
- [7] N. Wohnner, P. Lam, K. Sattler, *Carbon* **2014**, 67, 721.
- [8] H. E. Lim, Y. Miyata, R. Kitaura, Y. Nishimura, Y. Nishimoto, S. Irle, J. H. Warner, H. Kataura, H. Shinohara, *Nat. Commun.* **2013**, 4, 2548.
- [9] A. Omont, H. F. Bettinger, C. Tönshoff, *A&A* **2019**, 625, A41.
- [10] a) L. J. Allamandola, *EAS Publ. Ser.* **2011**, 46, 305; b) A. Tielens, L. J. Allamandola in *Physics and Chemistry at Low Temperatures* (Ed.: Khriachtchev), Pan Stanford Publishing, Boston, **2011**, pp. 341–380; c) A. G. G. M. Tielens, *Annu. Rev. Astron. Astrophys.* **2008**, 46, 289; d) A. G. G. M. Tielens, *Rev. Mod. Phys.* **2013**, 85, 1021; e) P. J. Sarre, *J. Mol. Spectrosc.* **2006**, 238, 1.
- [11] J. Lu, D. M. Ho, N. J. Vogelaar, C. M. Kraml, R. A. Pascal, *J. Am. Chem. Soc.* **2004**, 126, 11168.
- [12] S. Yamada, K. Kinoshita, S. Iwama, T. Yamazaki, T. Kubota, T. Yajima, K. Yamamoto, S. Tahara, *Org. Biomol. Chem.* **2017**, 15, 2522.
- [13] E. Clar, J. W. Wright, *Nature* **1949**, 163, 921.
- [14] a) C. Tönshoff, H. F. Bettinger, *Polyarenes I*, Springer, Heidelberg, **2013**, pp. 1–30; b) K. J. Thorley, J. E. Anthony, *Isr. J. Chem.* **2014**, 54, 642; c) J. E. Anthony, *Angew. Chem. Int. Ed.* **2008**, 47, 452; *Angew. Chem.* **2008**, 120, 460; d) J. E. Anthony, *Chem. Rev.* **2006**, 106, 5028.
- [15] M. Suzuki, T. Aotake, Y. Yamaguchi, N. Noguchi, H. Nakano, K.-i. Nakayama, H. Yamada, *J. Photochem. Photobiol. C* **2014**, 18, 50.
- [16] a) M. Watanabe, K.-Y. Chen, Y. J. Chang, T. J. Chow, *Acc. Chem. Res.* **2013**, 46, 1606; b) M. Watanabe, et al., *Nat. Chem.* **2012**, 4, 574.
- [17] a) R. Einholz, T. Fang, R. Berger, P. Grüninger, A. Früh, T. Chassé, R. F. Fink, H. F. Bettinger, *J. Am. Chem. Soc.* **2017**, 139, 4435; b) C. Tönshoff, H. F. Bettinger, *Angew. Chem. Int. Ed.* **2010**, 49, 4125; *Angew. Chem.* **2010**, 122, 4219; c) B. Shen, J. Tatchen, E. Sanchez-Garcia, H. F. Bettinger, *Angew. Chem. Int. Ed.* **2018**, 57, 10506; *Angew. Chem.* **2018**, 130, 10666.
- [18] a) J. Krüger, et al., *Angew. Chem. Int. Ed.* **2017**, 56, 11945; *Angew. Chem.* **2017**, 129, 12107; b) J. Krüger, et al., *ACS Nano* **2018**, 12, 8506; c) R. Zuzak, R. Dorel, M. Kolmer, M. Szymonski, S. Godlewski, A. M. Echavarren, *Angew. Chem. Int. Ed.* **2018**, 57, 10500; *Angew. Chem.* **2018**, 130, 10660; d) F. Eisenhut, T. Kühne, F. García, S. Fernández, E. Guitián, D. Pérez, G. Trinquier, G. Cuniberti, C. Joachim, D. Peña, F. Moresco, *ACS Nano* **2020**, 14, 1011.
- [19] A. M. Mastral, M. S. Callen, *Environ. Sci. Technol.* **2000**, 34, 3051.
- [20] B. Wen, K. K. Wang, *Pure Appl. Chem.* **2012**, 84, 893.
- [21] P. Makoš, A. Przyjazny, G. Boczkaj, *J. Chromatogr. A* **2018**, 1570, 28.
- [22] F. Zhang, Y. S. Kim, R. I. Kaiser, S. P. Krishtal, A. M. Mebel, *J. Phys. Chem. A* **2009**, 113, 11167.
- [23] D. Stahl, F. Maquin, *Chem. Phys. Lett.* **1984**, 108, 613.
- [24] L. Zhao, R. I. Kaiser, B. Xu, U. Ablikim, M. Ahmed, M. M. Evseev, E. K. Bashkurov, V. N. Azyazov, A. M. Mebel, *Angew. Chem. Int. Ed.* **2020**, 59, 4051; *Angew. Chem.* **2020**, 132, 4080.

Manuscript received: March 6, 2020

Accepted manuscript online: April 7, 2020

Version of record online: May 11, 2020