

Article

# Unlocking Acyclic #-Bond Rich Structure Space With Tetraethynylethylene–Tetravinylethylene Hybrids

Kelsey L. Horvath, Nicholas L. Magann, Madison J. Sowden, Michael G. Gardiner, and Michael S. Sherburn

J. Am. Chem. Soc., Just Accepted Manuscript • Publication Date (Web): 20 Nov 2019

Downloaded from pubs.acs.org on November 20, 2019

# Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.

is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

# Unlocking Acyclic *π*-Bond Rich Structure Space With Tetraethynylethylene–Tetravinylethylene Hybrids

Kelsey L. Horvath, ‡ Nicholas L. Magann, ‡ Madison J. Sowden, ‡ Michael G. Gardiner and Michael S. Sherburn\*

Research School of Chemistry, Australian National University, Canberra, ACT 2601 (Australia)

KEYWORDS hydrocarbons • polyenes • cross-coupling • carbon-rich materials

**ABSTRACT:** Literature reports describe tetraethynylethylene (TEE) as unstable but tetravinylethylene (TVE) as stable. The stabilities of these two known compounds are reinvestigated, along with those of five unprecedented TEE-TVE hybrid compounds. The five new  $C_{10}$  hydrocarbons possess a core, tetrasubstituted C=C bond carrying all possible combinations of vinyl and ethynyl groups. A unified strategy is described for their synthesis, whereupon cross-conjugated ketones are dibromo-olefinated then cross-coupled. Due to an incorrect but none-theless widely-held belief that acyclic  $\pi$ -bond rich hydrocarbons are inherently unstable, a standardized set of robustness tests is introduced. Whereas only TVE survives storage in neat form, all seven hydrocarbons are remarkably robust in dilute solution, generally surviving exposure to moderate heat, light, air and acid. The first X-ray crystal structure of TEE is reported. Sub-groups of hybrids based upon conformational preferences are identified through electronic absorption spectra and associated computational studies. These new acyclic  $\pi$ -bond rich systems have extensive, untapped potential for the production of stable, conjugated carbon-rich materials.

#### INTRODUCTION

Tetraethynylethylene (TEE, 1) and tetravinylethylene (TVE, 2), and their five hybrid structures 3-7 are amongst the smallest compounds that contain both through-conjugated and crossconjugated segments (**Figure 1**). The Diederich group disclosed the first synthesis of TEE 1 in 1991.<sup>1</sup> Separate studies<sup>2,3</sup> subsequently reported TEE 1 as unstable as a solid at 25 °C–even in the absence of O<sub>2</sub>–and caution has been expressed regarding the potential for explosive decomposition of TEE.<sup>4</sup> The first synthesis of TVE **2** was reported by Skattebøl and co-workers in the 1960s.<sup>5</sup> In 2014 we reported a one-step, multigram scale synthesis of TVE **2** involving the fourfold Stille coupling of tetrachloroethylene.<sup>6</sup> At the time, we noted the surprising stability of TVE **2**, which is a liquid that survives storage on the bench at ambient temperature and pressure.

TEE molecules with substituents at the four terminal alkyne positions are stable compounds.<sup>7</sup> In fact, the tetraphenyl analog was the first TEE compound to be prepared in 1967.<sup>8</sup> Many substituted analogues of TEE **1** have subsequently been prepared and studied, along with oligomeric TEE-based structures, expanded and cyclic systems, with much interest focused on their enormous potential in optical and electrical properties.<sup>9</sup> Recent reports describe Glasertype couplings of TEE **1** to prepare  $\beta$ -graphdiyne, a two dimensional carbon allotrope with predicted applications in energy storage and molecular electronics.<sup>10</sup>

Interest in designed carbon allotropes and associated (generally hydrocarbon-based) model molecular materials comprising *sp*<sup>2</sup> and *sp* carbons is rapidly expanding.<sup>11</sup> These efforts are focused on systems that rival the conducting, no band gap, "wonder material" graphene,<sup>12</sup> or exhibit specific band gaps required for devices such as semiconductors.



**Figure 1.** TEE **1** and TVE **2**, and the five possible hybrid structures **3-7** that define the structural possibilities between them. *Key*: TEVE = triethynylvinylethylene; DVDEE = divinyldiethynylethylene; TVEE = trivinylethynylethylene.

In contrast to the large, established body of important work focused on molecules carrying a TEE core, TVE **2** chemistry is in its infancy, with the first steps toward general synthetic approaches being published in 2014<sup>13</sup> and 2019.<sup>14</sup> These studies demonstrate that a compound with a tetravinylethylene unit serves as a hub for a sequence of up to four pericyclic reactions, each of which creates greater structural complexity. With a tetracycle and ten stereocenters generated through this process, TVE compounds have great potential in step- and atom-economic target synthesis.

The reported difference in stability between TEE **1** and TVE **2** is stark, and their projected applications are in divergent fields, namely functional materials and target synthesis. These facts prompted us to consider the structures that span the chasm of structural space

between TEE 1 and TVE 2: structures which define the most fundamental combinations of  $sp^2$  and sp carbons, hence serve as the foundations of applications in this field. Figure 1 depicts the five possible hybrids of TEE 1 and TVE 2, which feature both vinyl and ethynyl units attached to a tetrasubstituted central ethylene core. Structure 3 carries three ethynyl groups and one vinyl group, 7 carries three vinyl groups and one ethynyl group, and 4, 5 and 6 are the three constitutional and geometrical isomers carrying two ethynyl and two vinyl groups. Surprisingly, none of these five C10 hydrocarbons have been previously prepared. We devised a method to access compounds 3-7 for two reasons: firstly, in order to provide critical information about structure-stability/reactivity relationships of fundamental acyclic conjugated hydrocarbons; and secondly, to deliver a significantly greater variety of core C<sub>10</sub> structures to encourage applications of TEE and TVE-based structures in new materials and target synthesis.

Whereas the parent hydrocarbons 3-7 have not been prepared, we were encouraged by reports of stable, substituted derivatives of: (a) *E*-DVDEE **5** prepared by Diederich,<sup>15</sup> Nielsen<sup>16</sup> and Yamamoto;<sup>17</sup> (b) TEVE **3** by Hauptmann,<sup>18</sup> Diederich<sup>15d,15e,15g,19</sup> and Barluenga;<sup>20</sup> and (c) of cyclic substituted analogs of *gem*-DVDEE **6** described by Hopf.<sup>21</sup> No substituted versions of *Z*-DVDEE **4** or TVEE **7** have been reported in the literature.

# **RESULTS AND DISCUSSION**

1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34 35

36 37

38

39

40

41

42 43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58 59

60

CAUTION: TEE 1 is explosive when in neat crystalline form (*vide infra*). We have not experienced issues with solutions of TEE 1 but workers should be cautious when handling this substance in any form. We recommend the generation of batches of < 5 mg and that TEE 1 be maintained in solution. Experienced laboratory researchers should wear appropriate PPE when working with this compound and ensure it remains in a fume hood behind a blast shield, as a precaution.

Samples of TEE **1** and TVE **2** were prepared by literature methods, involving one flask, fourfold cross-couplings of tetrachloroethylene with vinyl and ethynyl nucleophiles.<sup>4,6,22</sup> In principle, stepwise sequential couplings with the same vinyl and ethynyl nucleophiles would permit the synthesis of the new hydrocarbons **3-7**. The requisite selective cross-couplings of tetrahaloethylenes, however, continue to prove elusive.<sup>13</sup>

The approach that ultimately proved successful (Scheme 1) involved twofold cross-couplings of 1,1-dibromoalkenes. We were inspired by the pioneering work of the Diederich group, who developed this method to prepare substituted TEEs.<sup>15,19</sup> We have previously used this process for the synthesis of substituted dendralenes<sup>23</sup> and TVEs.<sup>14</sup> On face value, therefore, the synthesis appears to be trivial. Closer inspection, however, reveals that unprecedented cross-coupling processes must be pioneered in order to achieve a synthesis of hybrids 3-7 using this approach. Firstly, whereas twofold sp-sp<sup>2</sup> cross-couplings of 1,1-dialkynyl-2,2dibromoethylenes 8 into TEEs 9, and twofold  $sp^2-sp^2$  crosscouplings of 1,1-dialkenyl-2,2-dibromoethylenes 10 into TEEs 11 are known, there are no examples of gem-DVDEE (12) syntheses from 1,1-dialkynyl-2,2-dibromoethylenes 8.24 Secondly, whereas 1alkynyl-1-alkenyl-2,2-dibromo-ethylenes 13 are known,<sup>25</sup> there are no examples of cross coupling reactions involving them. Thirdly, whilst we have recently reported the stereoselective synthesis of [3] dendralenes 18/19 from 1,1-dibromo-1,3-butadienes 16 by way of 3-bromotrienes 17,23 the conversion of 1-alkynyl-1-alkenyl-2,2dibromoethylenes 13 into Z- and E-DVDEE 20 and 21 would provide new insights into selective cross-coupling reactions. This approach raised several pertinent questions. Firstly, was monocoupling of dibromide **13** feasible? If so, would the bromine *cis*- to the alkenyl-substituent or the one *cis*- to the alkynyl-substituent be replaced by a new C–C bond? Finally, if selective mono-coupling could be achieved, would it be possible to steer the outcome of the second coupling to obtain each geometrical isomer, **20** and **21**?

With the main strategy defined and potential issues identified, one final tactical decision was made. We identified the TIPS- or TMS-protected terminal alkyne derivative of the C<sub>10</sub> hydrocarbon as the primary target, and perform a final stage desilylation to obtain the hybrid molecule **3-7**. We adopted this approach since it was presumed that the trialkylsilylated derivatives would be both less volatile and more stable than the corresponding hydrocarbon **3-7**. This prediction, which extrapolates information from literature reports of trialkylsilylated TEE derivatives,<sup>1,2,3,4</sup> proved to be correct.

# Scheme 1. The new transformations under scrutiny (shaded) and the closest precedent to them (unshaded).



Syntheses of the five new TEE-TVE hybrid hydrocarbons 3-7 are depicted in **Scheme 2**. *gem*-DVDEE **6** was prepared by a route involving a twofold Negishi cross-coupling of known dibromide  $22^{15a}$  with vinylzinc bromide. Dibromides **24** and **25**, prepared by

Ramirez dibromo-olefination of reported cross-conjugated ketone precursors,<sup>26</sup> were key intermediates *en route* to the four other TEE-TVE hybrids **3**, **4**, **5** and 7. TVEE 7 and TEVE **3** were prepared by the now familiar twofold coupling reaction from TIPS precursor **24**, in the former case a Negishi coupling with vinylzinc bromide and in the latter case a Sonogashira process with TMS-acetylene.

The final two hybrids, Z-DVDEE **4** and *E*-DVDEE **5** were the most challenging to prepare and, as detailed above, required the development of the most interesting chemistry. Dibromide **25** underwent a selective cross-coupling with vinylzinc bromide at the bromine *cis*- to the existing vinyl group, generating bromotrienyne **28**. In a subsequent reaction catalyzed by  $[Pd_2(dba)_3]/t$ -Bu<sub>3</sub>P, this compound underwent Negishi coupling with the organozinc reagent derived from TMS-acetylene to furnish *Z*-configured triene-diyne **29**, the product of stereoretention. With  $[PdCl_2(dppf)]$  as precatalyst, the same precursor **28** underwent a Sonogashira coupling with TMS-acetylene to give *E*-isomer **5**, the product of stereorinversion.

Scheme 2. Synthesis of TEE 1, TVE 2 and hybrids 3-7.



The conversion of dibromodienyne **25** into bromotrienyne **28** is unprecedented: there are neither examples of substrates of this type in the literature, nor couplings akin to this.<sup>27</sup> We propose that  $\pi$ complexation of Pd(0) with the adjacent vinyl group promotes oxidative insertion into the *cis*-disposed C–Br bond. Either  $\pi$ complexation to the rival C≡C bond of **25** is sterically disfavored by the presence of the TMS group, or the resulting  $\pi$ -complex positions the Pd(0) species less optimally for oxidative insertion.

While a stereoinvertive Negishi coupling of an alkynylzinc bromide with a 2-bromo-1,3-butadiene has been reported,<sup>28</sup> both the stereoinvertive Sonogashira coupling of  $28 \rightarrow 30$  and the stereoretentive Negishi coupling of  $28 \rightarrow 29$  are without precedent. We propose that these cross-couplings are both catalyst-controlled and kinetically-controlled events which follow the general principles originally introduced by Negishi,<sup>28</sup> since neither 28 nor 29 isomerize on exposure to the conditions used for stereoinvertive Sonogashira coupling (i.e.  $28 \rightarrow 30$ ) in the absence of TMS acetylene. *Z*-bromotrienyne 28 is, however, converted into its *E*-stereoisomer by heating at 120 °C.<sup>22</sup>

Removal of the terminal alkyne TIPS groups from compounds **23**, **26** and **27** to give clean samples of the new hydrocarbons **6**, 7 and **3** required considerable experimentation, due to challenges from both product volatility and separation of the hydrocarbon from non-polar silicon-containing residues. Solid TBAF in diethyl ether gave the best outcome by minimizing product loss during the solvent removal phase of the workup. In addition, the use of Kishi's non-aqueous work up for TBAF reactions<sup>29</sup> was critical for success. In contrast, removal of the TMS groups from compounds **29** and **30** to give clean samples of new hydrocarbons **4** and **5** was relatively straightforward. An alternative Wittig olefination approach to *E*-DVDEE **5** that is inspired by the wealth of information provided by the Diederich group<sup>2</sup> is described in the SI, along with the lessons learned from a related, unsuccessful approach to *Z*-DVDEE **4**.

Hydrocarbons 1-7 were purified by flash chromatography and were fully characterized using standard methods. TEE 1 is a crystalline solid at room temperature and ambient pressure, with TVEE 3 being semi-solid and the remainder being oils. We have not been able to obtain crystals of hydrocarbons 2-7 suitable for single crystal X-ray analysis. We are, however, delighted to report the first X-ray crystal structure of TEE 1, using small needles obtained by evaporation from pentane solution<sup>30</sup> (Figure 2), which shows the near planar structure of the TEE 1 molecules (maximum C deviation 0.029(3) Å).



Figure 2. X-ray crystal structure of TEE 1 highlighting associations in the solid state through face-face  $\pi$ -stacking (3.459(3) Å) along the *b* axis (a) that is offset due to tilting (26.21(8)°). The stacks, in turn, arrange efficiently (b, viewed down the *b* axis) via two distinct types of CH/ $\pi$  interactions<sup>11</sup> (disorder is removed for clarity).

UV-vis absorption spectra of the seven hydrocarbons 1-7 are depicted in **Figure 3**, which shows three groups of molecules, which are color-coded accordingly: (1) in red, TVE  $2^{32}$  and compounds 6 and 7 which exhibit broad absorptions at 280-300 nm and 220-230 nm; (2) in blue, compounds 3, 4 and 5, which show two distinct, sharper absorption maxima between 300-320 nm and fine structure

in their absorptions around 220 nm; and (3) in black, TEE 1,<sup>32</sup> which exhibits a uniquely complex set of absorptions. The longer wavelength absorptions are attributable to the  $6\pi$  electron chromophores and the shorter wavelength ones (for compounds 2-7) to  $4\pi$  systems.<sup>33</sup>



Figure 3. UV-visible absorption spectra of hydrocarbons 1-7 (acetonitrile solvent, 23 °C).

Computational studies reveal that the group of three compounds which give rise to broad absorption bands (**2**, **6** and **7**, red in **Figure 3**) are distinct from those that give sharper spectra (**3**, **4** and **5**, blue in **Figure 3**). The lowest energy conformations of the five new hybrid structures were located computationally and are depicted in **Figure 4**.<sup>22</sup> The reported, non-planar calculated conformations of TVE **2**,<sup>13</sup> and the essentially in-plane molecular structure from the X-ray crystal structure analysis of TEE **1** (**Figure 2**) were replicated computationally. Three of the five hybrid structures, namely TEVE **3**, Z-DVDEE **4** and E-DVDEE **5** prefer a single, in-plane conformation (**Figure 4**, top). *gem*-DVDEE **6** and TVEE **7** prefer nonplanar conformations (**Figure 4**, bottom), with the latter being reminiscent of the calculated lowest energy conformation of TVE **2**.



Figure 4. MP2/cc-pVTZ lowest energy conformations of the five new hybrids and TVE. The three above the line are planar; the three below are non-planar.

All 1,3-butadiene residues in the three planar TEE-TVE hybrids 3, 4 and 5 are *s*-*trans*. Their preference for the conformations depicted in **Figure 4** is strong. For example, the second lowest energy conformation of TEVE 3 has a *skew s*-*cis* 1,3-butadiene (twisted 18°

from planarity) and lies a substantial 19.1 kJ/mol higher in energy than that shown in **Figure 4** (see the SI for details).

In the preferred,  $C_2$  symmetric conformation of *gem*-DVDEE **6**, the [3]dendralene (3-methylene-1,4-pentadiene) moiety adopts a *skew s-trans–s-trans* conformation, with the *skew s-trans–gauche* conformer only 4.1 kJ/mol higher in energy.<sup>34</sup> Interestingly, the parent [3]dendralene prefers the *skew s-trans–gauche* conformation over the *skew s-trans–s-trans* conformation by 3.7 kJ/mol. To cause this reversal in conformational preference, either the ethynyl substituents in *gem*-DVDEE **6** destabilize the *skew s-trans–gauche* conformer through steric buttressing, or perhaps the *skew s-trans–strans* conformation is stabilized through conjugation.

The lowest energy conformation of TVE **2** is non-planar and  $C_2$  symmetric, with each *gem*-divinyl group adopting a *skew s-trans-gauche* conformation.<sup>13</sup> The four vinyl groups are slanted in the same general direction relative to the average plane of the central C=C bond and its four attached carbons, which has the effect of placing the four methylene groups on the same face of the central alkene. TVEE 7 prefers a conformation which mimics that of TVE **2**, but with a *gauche*-oriented vinyl group replaced by an ethynyl unit. The second lowest energy conformer of TVEE **7** (see the SI for details) lies 8.5 kJ/mol higher in energy and has the orientations of the two vinyl groups of the *gem*-divinyl portion of the molecule reversed.

Thus, in summary, more well-defined UV-vis absorption spectra are generated by the less conformationally flexible molecules **2**, **6** and **7**, which strongly prefer a single in-plane conformation, whereas broad absorption bands result from molecules **3**, **4** and **5**, which have several conformations close in energy to the global minimum, none of which are planar.

As mentioned in the introduction, solid samples of TEE 1 are reported to be explosive. Our results confirm these accounts. On one occasion, a ca. 0.5 mg sample in an aluminum cap exploded while being carried in a gloved hand, leaving a charcoal-like dusting on the glove.<sup>35</sup> We assume that solid samples of TEE 1 undergo rapid exothermic intermolecular addition-polymerization, in a similar manner to that proposed for other polyynes and related systems.<sup>36</sup> TEE 1 stands alone amongst hydrocarbons 1-7 in this regard. We recommend extreme caution when handling this substance. TEE 1 should only be handled in dilute solution and not in the solid state. No such issues were encountered with the remaining hydrocarbons 2-7, which presumably is a manifestation of their higher  $C(sp^2)$ : C(sp) ratio, hence greater stability. Differential scanning calorimetry traces for neat samples of compounds 2-7 are included in the Supporting Information. TEVE 3 shows an exotherm peaking at the lowest temperature (62 °C), *E*-DVDEE 5 has the highest (166 °C) and the remainder fall in the range 99–110 °C.

There is an incorrect but widely-held assumption that  $\pi$ -bondrich acyclic hydrocarbons are inherently unstable. Evidently these compounds have the potential to react/decompose under a wide variety of conditions. We consider that exposure to light, heat, oxygen and acid are the most significant ones in a typical laboratory setting. Thus, we performed a series of systematic robustness tests<sup>37</sup> upon these compounds, both as neat samples and as dilute solutions in common solvents, in order to provide quantitative information on their survival. It is important to note that these studies are not focused on identifying the mechanisms and/or kinetics of specific decomposition processes. In many cases, neither decomposition products nor processes are easily identified. Instead, the primary purpose is to provide empirical experimental data that estab1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51 52

53

54

55

56

57

58 59

60

lishes conditions required for compound survival. The results of these tests are depicted in **Table S1**, and are divided into two broad classes: those performed on samples held in dilute solution and those performed on neat samples. Substrates that decompose in dilute solution will generally (but not always) involve processes that are first order in hydrocarbon, whereas dimerization/oligomerization/polymerization processes will be favored for neat samples.

The most obvious conclusion from **Table S1** is that samples of hydrocarbons 1-7 generally survive better in dilute solution than on neat storage. Nonetheless, whereas only TVE **2** survives storage as a neat sample at ambient pressure and room temperature, *all seven compounds* **1**–7 *can be stored in dilute solution with negligible decomposition*. Furthermore, with dilute solutions, only TEE **1** exhibits decomposition on exposure to air and only TVE **2** decomposes on exposure to mild acid.

Moderate levels of decomposition are observed upon storage of neat samples of hybrids 4-7, and the most alkyne-rich structures 1 and 3 show complete decomposition. Storage at -20 °C slows down the rate of decomposition but generally with insufficient effectiveness to permit long term storage in this manner.

Since each of the hydrocarbons 1-7 carries, in a Z-disposition about its central tetrasubstituted C=C unit: (a) a pair of  $-C \equiv CH$ groups; and/or (b) a pair of -HC=CH<sub>2</sub> groups; and/or (c) a  $-C \equiv CH$  group and a  $-HC = CH_2$  group, these systems can undergo Bergmann cycloaromatization, (triene)  $6\pi$ -electrocyclization and Hopf cycloaromatization, respectively.<sup>38</sup> To our knowledge, these are the first structures to contain the requisite functionality for competition between these three related reactions. The primary decomposition pathway of TVE 2, TVEE 7 and Z-DVDEE 4 on heating in dilute solution is  $6\pi$ -electrocyclization.<sup>22</sup> We have previously noted that the electrocyclization of TVE 2 is more facile than those of substrates lacking additional vinyl groups<sup>13</sup> and this trend is followed with substrates carrying ethynyl groups (thermal  $6\pi$ electrocyclizations generally require temperatures of  $\geq 140 \text{ °C}^{39}$ ). We presume that the faster electrocyclization of TVE 2 (complete conversion after 2 h at 120 °C) than Z-trienes 4 and 7 (ca. 25-30% conversion under the same conditions) is due, at least in part, to the presence of two equivalent Z-trienes in TVE 2.

Thermal Hopf cycloaromatizations of acyclic Z-dienynes usually need temperatures well in excess of 200 °C,<sup>40</sup> hence the stability of *E*-DVDEE **5** and *gem*-DVDEE **6** in dilute solution at 120 °C is expected. Bergman cycloaromatization of acyclic Z-enediynes<sup>41</sup> proceed at temperatures similar to Hopf electrocyclizations. Since the substrate with an internal competition between Bergman cycloaromatization and  $6\pi$ -electrocyclization, namely Z-DVDEE **4**, shows no sign of cycloaromatization, we assume that the mechanism of thermal decomposition of other molecules containing *Z*enediynes, specifically TEE **1** and TEVE **3**, does not involve this process.

The aforementioned  $6\pi$ -electrocyclization products are the only ones identified, with intractable mixtures of (presumably) polymeric products being formed in all other cases. We strongly suspect that these other decomposition pathways are initiated by electrophilic and radical additions to the hydrocarbons, and that these undesired pathways are promoted when samples are more concentrated. Evidence for this proposal comes in the form of exposure of neat samples of TVEE 7 to air and TFA. On bubbling air though a neat sample of TVEE 7, 66% decomposition of the hydrocarbon was witnessed after 10 minutes, and 90% decomposition was seen on exposure to TFA for 1 h. Negligible decomposition was seen for comparable exposures to dilute solutions of the hydrocarbon.

# CONCLUSION

In summary, the first chemical syntheses of five related throughconjugated/cross-conjugated  $C_{10}$  hydrocarbons has been achieved. These structures, along with those of TEE and TVE, represent the fundamental arrangements of  $sp^2$  and sp carbons in the majority of carbon-based conductors. As such, this work serves as a foundation for applications in this field.

The need to synthesize TVE-TEE hybrids has led to the development of unprecedented synthetic transformations of wider value to the community. Specifically, new regio- and stereoselective cross-coupling variations have been uncovered, which merit detailed analysis, optimization and generalization.

The stability of each the seven unsubstituted hydrocarbons has been documented experimentally through the implementation of a series of robustness tests, which will have broader value for those interested in preparing and deploying fundamentally new molecules.

The first X-ray crystal structure of TEE 1 has been obtained, and an explosive decomposition pathway for this molecule has been uncovered. TVE 2 is the only one of the seven hydrocarbons that can be stored as a neat sample at room temperature. Importantly, all seven hydrocarbons can be stored in dilute solution at room temperature in ambient light without fear of decomposition. Each of the five new hybrid hydrocarbons 3-7 are more stable than TEE 1 towards air, and more stable than TVE 2 towards acid. These findings demonstrate the manageable nature of these new substances.

The conformational behavior of the seven unsubstituted systems has been related to their UV-visible absorption spectra. Overall, the structural requirements for in-plane conformations, hence optimal conjugation, has been verified. This fundamental information is essential to the use of these structures in carbon-rich conducting materials.

This study represents the foundations upon which new carbonrich materials can be designed and constructed, and new acyclic  $\pi$ bond rich hydrocarbons can be exploited.

# ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: XXXXXXX. Full experimental details, characterization data, <sup>1</sup>H and <sup>13</sup>C NMR spectra, X-ray crystallographic and computational studies (PDF). X-ray crystal structure of substituted DVDEE **S16** (CCDC: 1942588) (CIF)

X-ray crystal structure of TEE, **1** (CCDC: 1942589) (CIF)

# **AUTHOR INFORMATION**

#### **Corresponding Author**

\* michael.sherburn@anu.edu.au ORCID Kelsey L. Horvath: 0000-0003-0297-6982 Nicholas L. Magann: 0000-0002-7278-6642 Madison J. Sowden: 0000-0002-9016-0889 Michael G. Gardiner: 0000-0001-6373-4253 Michael S. Sherburn: 0000-0001-5098-0703

# **Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. ‡These authors contributed equally.

#### **Funding Sources**

This work was supported by the Australian Research Council (DP160104322).

#### Notes

1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58 59

60

The authors declare no competing financial interest.

#### ACKNOWLEDGMENT

Molecular structures from single crystal X-ray analyses and computed structures were visualized using either CYLview 1.0b; C. Y. Legault, Université de Sherbrooke, 2009 (<u>http://www.cylview.org</u>) or X-Seed (L. J. Barbour, X-Seed - A software tool for supramolecular crystallog-raphy, *J. Supramol. Chem.* **2001**, **1**, 189-191).

#### ABBREVIATIONS

TEE, tetraethynylethylene; TVE, tetravinylethylene; TEVE, triethynylvinylethylene; DVDEE, divinyldiethynylethylene; TVEE, trivinylethynylethylene; TIPS, tri-isopropylsilyl; TMS, trimethylsilyl; dba, dibenzylideneacetone; dppf, 1,1'-bis(diphenylphosphino)ferrocene; TBAF, tetra-*n*-butylammonium fluoride; UV-vis, ultraviolet-visible; rt, temp temperature.

#### REFERENCES

<sup>1</sup> Y. Rubin, C. B. Knobler, F. Diederich, Tetraethynylethene, *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 698-700.

<sup>2</sup> J. Anthony, A. M. Boldi, Y. Rubin, M. Hobi, V. Gramlich, C. B. Knobler, P. Seiler, F. Diederich, Tetraethynylethenes: Fully cross-conjugated  $\pi$ -electron chromophores and molecular scaffolds for all-carbon networks and carbon-rich nanomaterials, *Helv. Chim. Acta* **1995**, *78*, 13-45.

<sup>3</sup> N. P. Bowling, R. J. McMahon, Enediyne isomers of tetraethynylethene, *J. Org. Chem.* **2006**, *71*, 5841-5847.

<sup>4</sup> O. F. Koentjoro, P. Zuber, H. Puschmann, A. E. Goeta, J. A. K. Howard, P. J. Low, A simple synthesis of tetraethynylethenes and representative molecular structures of some dicobalt derivatives *J. Organomet. Chem.* **2003**, *670*, 178-187.

<sup>5</sup> (a) L. Skattebøl, The synthesis of allenes from 1,1-dihalocyclopropane derivatives and alkyllithium, *Acta. Chem. Scand.* **1963**, *17*, 1683–1693; (b) L. Skattebøl, S. Solomon, Thermally induced reactions of some novel allenes, *J. Am. Chem. Soc.* **1965**, *87*, 4506–4513; (c) L. Skattebøl, J. L. Charleton, P. deMayo, Tetravinylethylene, *Tetrahedron Lett.* **1966**, *7*, 2257–2260.

<sup>6</sup> E. J. Lindeboom, A. C. Willis, M. N. Paddon-Row, M. S. Sherburn, Tetravinylethylene, *Angew. Chem. Int. Ed.* **2014**, *79*, 5440–5443.

<sup>7</sup> J. Anthony, A. M. Boldi, Y. Rubin, M. Hobi, V. Gramlich, C. B. Knobler, P. Seiler, F. Diederich, π-Electron chromophores and molecular scaffolds for all-carbon networks and carbon-rich nanomaterials *Helv. Chim. Acta* **1995**, *78*, 13-45.

<sup>8</sup> (a) J. Burdon, P. L. Coe, C. R. Marsh, J. C. Tatlow, Reactions of organo-copper compounds with halogeno-olefins, *Chem. Commun.* 1967, 1259-1260;
(b) Y. Hori, K. Noda, S. Kobayashi, H. Taniguchi, Synthesis and properties of tetrakis(phenylethynyl)ethylene, *Tetrahedron Lett.* 1969, 3563-3566; (c) H. Hopf, M. Kreutzer, P. G. Jones, New planar π-systems, II: on the preparation and structure of tetrakis(phenylethynyl)ethene, *Chem. Ber.* 1991, *124*, 1471-1475.

<sup>9</sup> Reviews: (a) R. R. Tykwinski, F. Diederich, Tetraethynylethene molecular scaffolding, *Liebigs Ann./Recl.* **1997**, 649-661; (b) F. Diederich, Carbonrich acetylenic scaffolding: rods, rings and switches, *Chem. Commun.* **2001**, 219-227; (c) M. B. Nielsen, F. Diederich, Functional conjugated materials for optonics and electronics by tetraethynylethene molecular scaffolding. In *Modern Arene Chemistry*, D. Astruc, Ed. Wiley-VCH: Weinheim, Germany, 2002; pp 196-216; (d) M. B. Nielsen, F. Diederich, Conjugated oligoenynes based on the diethynylethene unit, *Chem. Rev.* **2005**, *105*, 1837-1867.

<sup>10</sup> (a) J. Li, Z. Xie, Y. Xiong, Z. Li, Q. Huang, S. Zhang, J. Zhou, R. Liu, X. Gao, C. Chen, L. Tong, J. Zhang, Z. Liu, Architecture of β-graphdiynecontaining this film using modified Glaser-Hay coupling reaction for enhanced photocatalytic property of TiO<sub>2</sub>, *Adv. Mater.* **2017**, *29*, 1700421; (b) Z. Jia, Y. Li, Z. Zuo, H. Liu, D. Li, Y. Li, Carbon Ene-Yne. *Adv. Electron. Mater.* **2017**, *3*, 1700133; (c) J. Li, Y. Xiong, Z. Xie, X. Gao, J. Zhou, C. Yin, L. Tong, C. Chen, Z. Liu, J. Zhang, Template synthesis of an ultrathin β-graphdiynelike film using the Eglinton coupling reaction, *ACS Appl. Mater. Interfaces* **2019**, *11*, 2734-2739.

<sup>11</sup> M. D. Kilde, A. H. Murray, C. L. Andersen, F. E. Storm, K. Schmidt, A. Kadziola, K. V. Mikkelsen, F. Hampel, O. Hammerich, R. R. Tykwinski, M. B. Nielsen, Synthesis of radiaannulene oligomers to model the elusive carbon allotrope 6,6,12-graphyne, *Nat. Commun.* **2019**, *10*, 3714.

<sup>12</sup> A. K. Geim, K. S. Novoselov The rise of graphene, *Nat. Mat.* **200**7, *6*, 183–191.

<sup>13</sup> E. J. Lindeboom, A. C. Willis, M. N. Paddon-Row, M. S. Sherburn, Computational and synthetic studies with tetravinylethylenes, *J. Org. Chem.* **2014**, 53, 11496–11507.

<sup>14</sup> K. L. Horvath, C. G. Newton, K. A. Roper, J. S. Ward, M. S. Sherburn, A broad-spectrum synthesis of tetravinylethylenes, *Chem. - Eur. J.* **2019**, *25*, 4072-4076.

<sup>15</sup> (a) A. M. Boldi, J. Anthony, C. B. Knobler, F. Diederich, Novel crossconjugated compounds derived from tetraethynylethene, Angew. Chem., Int. Ed. Engl. 1992, 31, 1240-1242; (b) J. Anthony, C. B. Knobler, F. Diederich, Stable [12]- and [18]Annulenes derived from tetraethynylethene, Angew. Chem., Int. Ed. Engl. 1993, 32, 406-409; (c) J. Anthony, C. Boudon, F. Diederich, J. P. Gisselbrecht, V. Gramlich, M. Gross, M. Hobi, P. Seiler, Stable soluble conjugated carbon rods with a persilylethynylated polytriacetylene backbone, Angew. Chem., Int. Ed. Engl. 1994, 33, 763-766; (d) J. Anthony, A. M. Boldi, Y. Rubin, M. Hobi, V. Gramlich, C. B. Knobler, P. Seiler, F. Diederich, Tetraethynylethenes: fully cross-conjugated  $\pi$ -electron chromophores and molecular scaffolds for all-carbon networks and carbon rich nanomaterials, Helv. Chim. Acta 1995, 78, 13-45; (e) R. R. Tykwinski, M. Schreiber, R. Perez Carlon, F. Diederich, V. Gramlich, Donor/acceptorsubstituted tetraethynylethenes: systematic assembly of molecules for use as advanced materials, Helv. Chim. Acta 1996, 79, 2249-2281; (f) J.-F. Nierengarten, M. Schreiber, F. Diederich, V. Gramlich, Novel extended πchromophores based on tetraethynylethene, New J. Chem. 1996, 20, 1273-1284; (g) L. Gobbi, P. Seiler, F. Diederich, V. Gramlich, C. Boudon, J.-P. Gisselbrecht, M. Gross, Photoswitchable tetraethynylethene-dihydroazulene chromophores, Helv. Chim. Acta 2001, 84, 743-777.

<sup>16</sup> (a) M. B. Nielsen, J.-P. Gisselbrecht, N. Thorup, S. P. Piotto, C. Boudon, M. Gross, Synthesis and characterization of alkene-extended tetrathiafulvanes with lateral alkyne appendages, *Tetrahedron Lett.* **2003**, *44*, 6721-6723; (b) A. S. Andersson, K. Qvortrup, E. R. Torbensen, J.-P. Mayer, J.-P. Gisselbrecht, C. Boudon, M. Gross, A. Kadziola, K. Kilsa, M. B. Nielsen, Synthesis and characterization of extended tetrathiafulvalenes with di-, tri-, and tetraethynylethene cores, *Eur. J. Org. Chem.* **2005**, 3660-3671.

<sup>17</sup> (a) D. H. Camacho, S. Saito, Y. Yamamoto, Synthesis of (E)-1,2-divinyl-1,2-diethynylethene (DVDEE) via the palladium catalyzed reaction of conjugated diynes. A new building block for molecular scaffolding. *J. Am. Chem. Soc.* **2002**, *124*, 924-925; (b) N. K. Pahadi, D. H. Camacho, I. Nakamura, Y. Yamamoto, Palladium-catalyzed dimerization of conjugated diynes: synthesis of (E)-1,2-divinyldiethynylethenes having donor and acceptor chromophores at the terminus of alkyne, *J. Org. Chem.* **2006**, *71*, 1152-1155.

<sup>18</sup> (a) H. Hauptmann, Untersochongen zu baseninduzierten reaktionen an tetraathinylathamene, *Tetrahedron Lett.* **1975**, 1931-1934; (b) H. Hauptmann, M. Mader, Reduktive cyclisierungen am (*Z*)-3-hexen-1,5-diin-systme – zur darstellung des 2,3,6,7-tetra-tert-butylnaphthalins, *Tetrahedron Lett.* **1980**, *21*, 897-898.

<sup>19</sup> F. Bures, W. B. Schweizer, J. May, C. Boudon, J.-P. Gisselbrecht, M. Gross, I. Biaggio, F. Diederich, Property tuning in charge-transfer chromo-

1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

60

<sup>20</sup> J. Barluenga, D. de Saa, A. Gomez, A. Ballesteros, J. Santamaria, A. de Prado, M. Tomas, A. L. Suarez-Sobrino, Metal carbene dimerization: versatile approach to polyalkynylethenes, *Angew. Chem. Int. Ed.* **2008**, *47*, 6225-6228.

<sup>21</sup> H. Hopf, J. Kampen, P. Bubenitschek, P. G. Jones, En route to 7,7,8,8-tetraethynyl-*p*-quinodimethane (TEQ), *Eur. J. Org. Chem.* **2002**, 1708-1721.

<sup>22</sup> See the Supporting Information for details.

<sup>23</sup> M. S. Sherburn, J. George, J. S. Ward, A General Synthesis of Dendralenes. *Chem. Sci.* DOI: 10.1039/c9sc03976g

<sup>24</sup> In principle, twofold  $sp-sp^2$  cross-couplings of 1,1-dialkenyl-2,2dibromoethylenes **10** could also be used here. Challenges with the preparation of the parent 1,1-divinyl-2,2-dibromoethylene caused us to focus on this alternative approach.

<sup>25</sup> (a) A. L. K. Shi Shun, E. T. Chernick, S. Eisler, R. R. Tykwinski, Synthesis of unsymmetrically substituted 1,3-butadiynes and 1,3,5-hexatriynes via al-kylidene carbenoid rearrangements, *J. Org. Chem.* 2003, *68*, 1339-1347; (b) A. L. K. S. Shun, R. R. Tykwinski, Synthesis of naturally occurring acetylenes via an alkylidene carbenoid rearrangement, *J. Org. Chem.* 2003, *68*, 6810-6813; (c) P. Bichler, W. A. Chalifoux, S. Eisler, A. L. K. Shi Shun, E. T. Chernick, R. R. Tykwinski, Mechanistic aspects of alkyne migration in alkylidene carbenoid rearrangements, *Org. Lett.* 2009, *11*, 519-522.

<sup>26</sup> (a) M. Malacria, M. L. Roumestant, Vinylallenes—VI : Synthese de cetones de la serie de la jasmine, *Tetrahedron* **1977**, 33, 2813-2817; (b) H.-S. Yeom, Y. Lee, J. Jeong, E. So, S. Hwang, J.-E. Lee, S. S. Lee, S. Shin, Stereoselective one-pot synthesis of 1-aminoindanes and 5,6-fused azacycles using a gold-catalyzed redox-pinacol-Mannich-Michael cascade, *Angew. Chem. Int. Ed.* **2010**, *49*, 1611-1614.

<sup>27</sup> Selective single couplings of *aldehyde-derived* 1,1-haloalkenes have been widely reported, with the bromine *cis*- to the alkene C–H bond being replaced. First reports: (a) A. Minato, K. Suzuki, K. Tamao, A remarkable steric effect in palladium-catalyzed Grignard coupling: regio- and stereoselective monoalkylation and -arylation of 1,1-dichloro-1-alkenes, *J. Am. Chem. Soc.* 1987, *109*, 1257-1258; (b) B. M. Trost, R. Walchli, A novel palladium catalyzed reductive cyclization, *J. Am. Chem. Soc.* 1987, *109*, 3487-3488; (c) V. Ratovelomanana, A. Hammoud, G. Linstrumelle, Selective palladium-catalysed substitution of 1,1-dichloroethylene, *Tetrahedron Lett.* 1987, *28*, 1649-1650; (d) W. R. Roush, R. Riva, Enantioselective synthesis of the bottom half of chlorothricolide. 2. A comparative study of substituent effects on the stereoselectivity of the key intramolecular Diels-Alder reaction, *J. Org. Chem.* 1988, *53*, 710-712.

<sup>28</sup> Stereo-retentive and stereo-invertive Negishi couplings of 2-bromo-1,3butadienes are known: (a) X. Zeng, Q. Hu, M. Qian, E. Negishi, Clean inversion of configuration in the Pd-catalyzed cross-coupling of 2-bromo-1,3dienes *J. Am. Chem. Soc.* **2003**, *125*, 13636-13637; (b) X. Zeng, M. Qian, Q. Hu, E. Negishi, Highly stereoselective synthesis of (1E)-2-methyl-1,3-dienes by palladium-catalyzed *trans*-selective cross-coupling of 1,1-dibromo-1-alkenes with alkenylzinc reagents *Angew. Chem. Int. Ed.* **2004**, *43*, 2259-2263; (c) reference 23.

<sup>29</sup> Y. Kaburagi, Y. Kishi, Operationally simple and efficient workup procedure for TBAF-mediated desilylation: application to halichondrin synthesis, *Org. Lett.* **200**7, *9*, 723-726.

<sup>30</sup> The crystals examined decompose over minutes at ambient temperature. They were brought to the microscope cold and selection was done within a minute or so at ambient temperature with partial coloration of the crystals. After ca. 5 mins at ambient temperature they no longer diffracted. A number of crystals were mounted, screened and stored in liquid nitrogen between screening attempts. This allowed the best crystal to be chosen. The needleshaped crystals each showed evidence of twinning/not being single which could not be handled with twinning routines. Nevertheless, the diffraction data of the main component yielded good quality metrics, albeit the small crystals diffracted only to moderate resolution with long collection times. See the following section of the main text of the manuscript for further information on the stability of TEE 1.

 $^{31}$  For related CH/ $\pi$  interactions, see: (a) T. S. Thakur, R. Sathishkumar, A. G. Dikundwar, T. N. Guru Row, G. R. Desiraju, Third polymorph of phenylacetylene, *Cryst. Growth Des.* **2010**, *10*, 4246-4249; (b) M. T. Kirchner, D. Bläser, R. Boese, Co-crystals with acetylene: small is not simple! *Chem. Eur. J.* **2010**, *16*, 2131-2146.

 $^{32}$  These UV-vis spectra are consistent with those previously reported. For TVE **2**, see reference 6; for TEE **1**, see reference 1.

<sup>33</sup> (a) *E*- and *Z*-1,3,5-hexatrienes show three absorptions at 245, 255 and 265 nm: (J. C. H. Hwa, P. L. de Benneville, H. J. Sims, New preparation of 1,3,5-hexatriene and the separation of its geometrical isomers, *J. Am. Chem. Soc.* **1960**, *82*, 2537-2540); (b) *E*- and *Z*-hexa-1,5-diyn-3-enes show two absorptions at 250 and 262 nm (W. H. Okamura, F. Sondheimer, 1,3,7,9,13,15-Hexadehydro[18]annulene, *J. Am. Chem. Soc.* **1967**, *89*, 5991-5992); (c) hexa-1,3-dien-5-yne gives a single absorption at 252 nm (F. Sondheimer, D. A. Ben-Efraim, Y. Gaoni Unsaturated macrocyclic compounds. XVIII.<sup>1</sup> The prototropic rearrangement of linear 1,5-diynes to conjugated polyen-ynes, *J. Am. Chem. Soc.* **1961**, *83*, 1682-1685).

<sup>34</sup> M. F. Saglam, T. Fallon, M. N. Paddon-Row, and M. S. Sherburn Discovery and computational rationalization of diminishing alternation in [*n*]dendralenes, *J. Am. Chem. Soc.* **2016**, *138*, 1022-1032.

<sup>35</sup> CAUTION: TEE **1** is explosive when in neat crystalline form. We strongly recommend that only small quantities be generated and that the compound is handled in solution to minimize the hazard of this highly reactive compound. Only ca. 0.5 mg was being handled at the time of the explosion and the worker was not harmed. We presume that heat from the worker's hand was involved in the rapid decomposition process. NMR and MS analysis of the residue gave no evidence for the formation of fullerenes.

<sup>36</sup> (a) R. H. Baughman, Dangerously seeking linear carbon, *Science*, **2006**, 312, 1009-1110; (b) W. A. Chalifoux, R. R. Tykwinski, Synthesis of polyynes to model the *sp*-carbon allotrope carbyne *Nat. Chem.* **2010**, 2, 967–971; (c) K. S. Feldman, C. K. Weinreb, W. J. Youngs, J. D. Bradshaw, Preparation and some subsequent transformations of tetraethynylmethane *J. Am. Chem. Soc.* **1994**, *116*, 9019-9026.

<sup>37</sup> For precedent showing stability testing, see Bryce and co-workers: K. West, C. Wang, A. S. Batsanov, M. R. Bryce. Are terminal aryl butadiyne stable? Synthesis and X-ray crystal structures of a series of aryl- and heteroaryl-butadiynes (Ar-C=C-C=C-H), *J. Org. Chem.* **2006**, *71*, 8541-8544. This proposal is inspired by work by Collins and Glorius, who introduced a method to evaluate the broadness of applicability of new synthetic transformations: K. D. Collins, F. Glorius, A robustness screen for the rapid assessment of chemical reactions, *Nat. Chem.* **2013**, *5*, 597–601.

<sup>38</sup> For an excellent, general review of these and related reactions, see R. K. Mohamed, P. W. Peterson, I. V. Alabugin, , Concerted reactions that produce diradicals and zwitterions: electronic, steric, conformational, and kinetic control of cycloaromatization processes, *Chem. Rev.* **2013**, *113*, 7089-7129.

<sup>39</sup> Review: M. Shindo, T. Yoshikawa, K. Yaji, Synthesis of 1,3-dienes by cycloaddition and electrocyclic reactions, in *Science of Synthesis, Vol. 46*, **2009**, pp. 353-400.

<sup>40</sup> (a) H. Hopf, H. Musso, Preparation of benzene by pyrolysis of *cis*- and *trans*-1,3-hexadien-5-yne, *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 680; (b) review: G. Zimmermann, Open and masked 1,3-hexadien-5-ynes – mechanistic and synthetic aspects, *Eur. J. Org. Chem.* **2001**, 457-471.

<sup>41</sup> (a) R. R. Jones, R. G. Bergman, *p*-Benzyne. Generation as an intermediate in a thermal isomerization reaction and trapping evidence for the 1,4benzenediyl structure, *J. Am. Chem. Soc.* **1972**, *94*, 660- 661; (b) review: M. Kar, A. Basak, Design, Synthesis, and biological activity of unnatural enediynes and related analogues equipped with pH-dependent or phototriggering devices, *Chem. Rev.* **2007**, *107*, 2861-2890. Toc graphic:

Z-DVDEE E-DVDEE TEE TEVE TVEE gem-DVDEE