Article

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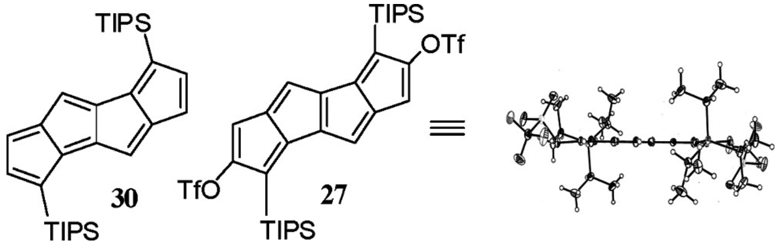

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Synthesis of Dicyclopenta[*a*,*e*]pentalenes via a Molybdenum Carbonyl Mediated Tandem Allenic Pauson−Khand Reaction and the X-ray Crystal Structure of a Planar Dicyclopenta[*a*,*e*]pentalene

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Abstract: Two 14 π cross-linked annulenes which belong to the family of dicyclopenta[*a*,*e*]pentalenes have been synthesized, 14 π bis enol triflate ester **27** and the 3,7-diisopropylsilyl substituted 14 π dicyclopenta-[*a*,*e*]pentalene **30**. The new allenic tandem Pauson−Khand reaction mediated by $Mo(CO)_6$ was employed as the key process to construct the core of the tetracycles. The two linear dicyclopenta[*a*,*e*]pentalenes **27** and **30** underwent significant electronic delocalization, perhaps even aromaticity, as revealed by the X-ray structure of **27**. The tetracyclic rings in **27** assumed a flat geometry (Figure 4); the bond lengths of the tetracycle in **27** also fit well into the criteria for aromatic compounds. A comparison of the NMR and UV spectra of both **27** and **30** demonstrated that they both exhibited similar electronic properties, therefore, the purple colored 14 π cross linked annulene **30** is planar as well as delocalized.

Introduction

Dicyclopenta[*a*,*e*]pentalene **1** and dicyclopenta[*a*,*f*]pentalene **2** have not been synthesized and have been discussed only from a computational point of view (Figure 1). Controversey exists as to whether these 14 π cross linked annulenes are delocalized, exhibit aromatic Hückel "type" stability or exist as nonalternant hydrocarbons that behave as highly reactive olefins. Both of these molecules can be envisioned as a pentalene fused to a fulvene or two pentalenes fused together. Pentalene has been shown to be highly unstable,[1] moreover, fulvenes are also unstable.[1] However, both cyclopentapentalenes **1** and **2** are 14 π cross linked annulenes. If the Hückel rule can be applied here, then both **1** and **2** should show some delocalization and perhaps even aromatic character as found in the case of azulene. In addition, one can also envisage stabilization of the central pentalene unit by overlap with the two pendant cyclopentadienes. It is important to point out that both **1** and **2** are linear cross-linked annulenes. Not much work on the chemical character of linear cross-linked annulenes has appeared previously.

Renewed interest in the stability of cyclopentapentalenes **1** and **2** has recently appeared. Nakajima and Toyota[2,3] have reported theoretical calculations on these two cross linked annulenes. On the basis of semiempirical self-consistent field molecular orbital theory, **1** and **2** were examined for the most favorable ground-state geometrical structures (energetically) with respect to C−C bond lengths. This older method provided resonance energy values for a given annulene and was applied to azuleno[1,2-*b*]azulene in which good agreement with experimental data was found. If dicyclopenta[*a*,*e*]pentalene **1** and dicyclopenta[*a*,*f*]pentalene **2** exhibit aromatic character as postulated, then the resonance energy for the linear **1** was computed to be 6.8 kcal/mol compared to 1.2 kcal/mol for **2**. These results are in contrast to the work of Hess and Schaad,[4,5] who employed Hückel molecular orbital theory. They reported that both cross-linked annulenes would be antiaromatic with heptaene **2** exhibiting more delocalization of π electrons than **1**. Glidewell and Lloyd have employed SCF calculations which suggested strong fixation of the double bonds in **1** but that **1** should still be lower in energy than **2**.[6] According to Parr, et al.[7] however, when relative hardness (HOMO−LUMO gap) was employed as a measure of aromatic stability, **2** should be more stable than **1**. Ab initio calculations in our own laboratory at the 6-31G* basis set[8] indicated **2** should be slightly more stable

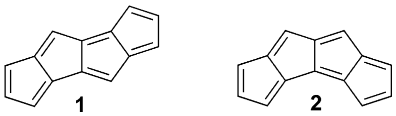
1 2

Figure 1. Dicyclopenta[*a*,*e*]pentalene **1** and dicyclopenta[*a*,*f*]pentalene **2**.

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† Department of Chemistry, University of Wisconsin−Milwaukee.

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than **1** by 0.33 kcal/mol. In addition, in the early 1970s, Balaban reported,[9] in a theoretical sense, the Hückel rule cannot be extended to the cata-condensed alternate or nonalternate polycyclic hydrocarbons which included the 14 π system **1**, because these polycyclic hydrocarbons do not possess a closed electronic shell. Furthermore, he also concluded these systems cannot be regarded as bridged annulenes, for truly bridged cross-linked annulenes contain bridges with more than one single bond.[9] More recently, he suggested that these two molecules (**1** and **2**) could not be considered as aromatic,[10] because they contain an "abnormal HOMO−LOMO situation" (bonding orbitals are vacant or antibonding orbitals are occupied),[11] although they both contain odd numbers of double bonds.[9−11]

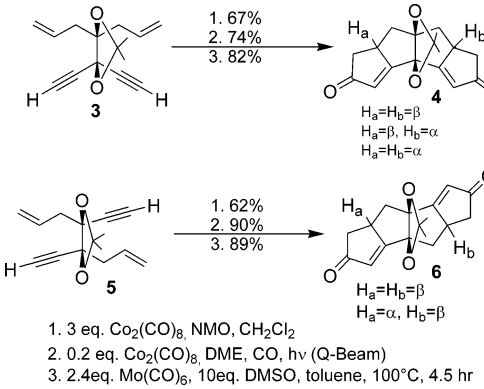
Although electronic delocalization may play a role in the preparation and isolation of 14 π cross linked annulenes such as dicyclopenta[*a,e*]pentalene **1** and dicyclopenta[*a,f*]pentalene **2**, certainly the olefinic intermediates (cyclopentadienes) toward these polyquinenes are expected to be highly reactive.

A tetra-*tert*-butyl derivative of **1** was prepared and isolated by Hafner et al.,[12] as well as examined, spectroscopically. Based on the ^{1}H NMR studies, the double bonds in this tetra-*tert*-butyl dicyclopenta[*a,e*]pentalene were proposed fixated in agreement with the SCF calculations of Nakajima and Toyota.[12] The ring protons appeared significantly upfield from the aromatic region; however, the proton signals were downfield with respect to the olefinic region which suggest some resonance delocalization, albeit minor. Herein, is described the synthesis of two 14π systems **27** and **30** which belong to this family of cross linked annulenes, including analysis of the structures of these two molecules by NMR and UV spectroscopy as well as X-ray analysis. Studies indicated these two 14π cross linked annulenes (**27** and **30**) demonstrated aromatic delocalization, which was significantly different from that for the tetra-*tert*-butyl substituted analogue reported by Hafner et al.[12]

Synthesis of Dicyclopentapentalenes 27 and 30.[13] The parent ring systems of **1** and **2** have been prepared by Eaton,[14,15] McKervey,[16] Kotha,[17] Mehta[18,19]and others, as well as in our laboratory.[20] Recently, a new approach to these molecules has been designed and executed which employed a tandem Pauson-Khand reaction to regiospecifically generate the tetracyclic framework of cross linked annulenes **1** and **2**. [21−25] This work provided systems required for the construction of **1** and **2** in a higher oxidation state than those achieved previously.[24]

The required bisalkene−bisalkynes **3** and **5** illustrated in Scheme 1 could be accessed on large scale. [24,29] The tetracylic ring systems **4** and **6** could also be synthesized rapidly on gram-scale; however, Van Ornum had recently shown it was difficult to isolate a tetraene (a dicyclopentadiene) related to **4**.[26] Sodium borohydride reduction had provided the corresponding diol, but attempts to convert this diol into a tetraene via an acid-catalyzed elimination proved impractical.[26] Although related tetraenes had been observed by ^{1}HNMR spectroscopy,[26] attempts at isolation had resulted in polymerization or decomposition. Either the cyclopentadienes were too unstable or the acetonide began to decompose, consequently, this approach was modified.[26,29]

Scheme 1



It was decided to stabilize the cyclopentadiene substituents with bulky groups, analogous to the previous approach of Hafner et al.[12] In addition, although the stereocenters in **4** and **6** would eventually be destroyed, it might be difficult to carry the mixture on in succeeding steps. Moreover, one might choose a precursor in a higher oxidation state closer in energy to the target 14 π cross linked annulene. This would provide a tetracycle which would require fewer high energy steps to approach the target than previously envisaged. [21−25]

In a retrosynthetic sense, if a bisallene-bisalkyne **8** (Figure 2) could be synthesized, then it might be coerced to cyclize to provide a new tetracycle **7** via an allenic version of the tandem Pauson−Khand reaction. On comparison of the new intermediate, tetracycle **7,** with the former tetracycles **4** and **6**, the advantages were obvious. The new tetracycle **7** would be

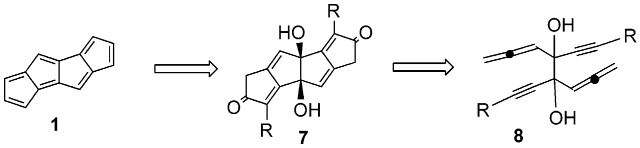


Figure 2. Retrosynthetic analysis via the bisallene **8**.

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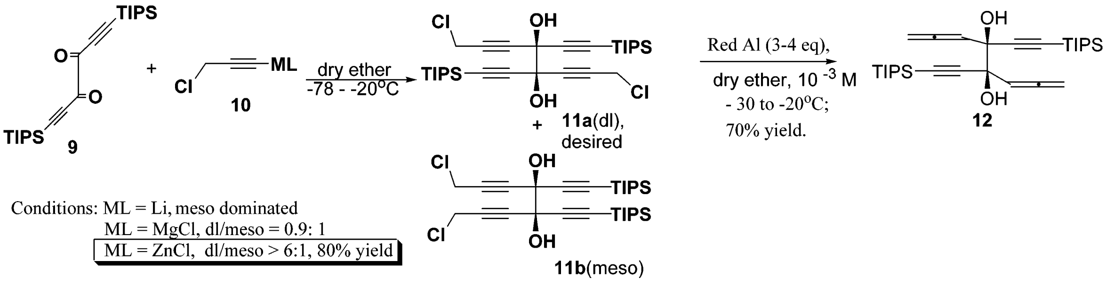
Scheme 2



obtained as only one stereoisomer, instead of a mixture of two or three diastereomers. Moreover, two additional units of unsaturation would be incorporated into the tetracycle **7** (vs **4** and **6**), at an earlier stage.

In this vain, Brummond et al.[27,28] had recently reported a molybdenum hexacarbonyl mediated allenic Pauson−Khand reaction in the conversion of an allene-alkyne into the cyclopentenone. Importantly, if there was a two-carbon link between the reactive allene and alkyne moieties, as in the case of bisallene-bisalkyne **8**, the process selectively underwent cyclization with the terminal double bond of the allene. The exact situation required to prepare tetraene **7**.

The synthesis of the bisallene-bisalkyne **8** then took center stage. After a few attempts,[29] the desired (±)-diol **12** was obtained via the procedure illustrated in Scheme 2. The tetraalkyne **11** was synthesized by treatment of the 1,2-diketone **9**[25,30] with the alkynylide of propargyl chloride. The propargyl chloride was stirred with butyllithium in diethyl ether at −78 °C to produce the alkynylide anion **10** (the lithium anion survived only at low temperature[31]). Zinc proved to be the best choice as the metal counterpart of the alkynylide anion with respect to stereoselectivity and yield (Scheme 2). A similar effect had been observed previously by the authors in another system.[25] When lithium was employed directly (M = Li) in this process, the yield was low and the undesired meso isomer **11b** predominated. When magnesium was employed, this reaction provided the tetrayne **11** in moderate yield with almost no stereoselectivity (**11a**:**11b** = 0.9:1). Meso selectivity was also observed by Diederich et al.,[32] when trimethylsilyl acetylenyl magnesium was reacted with the same 1,2-diketone **9**.

However, when zinc was employed as the metal counterpart to stabilize the carbanion (produced by treating the lithium alkynylide of propargyl chloride with anhydrous $ZnCl_2$ at low temperature), the yield increased to over 80% and the desired dl diastereomer **11a** predominated in a ratio of 6:1 over the meso isomer **11b**. To date, the Felkin−Anh model[33,34] of addition can be employed to rationalize the observed stereoselectivity of the zinc-mediated process in Scheme 2 (see Supporting Information for more details).

Lithium aluminum hydride has been reported in the literature[35] as the reagent of choice to convert propargyl chlorides into allenes. Unfortunately, when the tetrayne **11a** was treated under the reported conditions,[35] a complex mixture of products was obtained with the desired bisallene-bisalkyne **12** present in very low yield. A number of other hydride sources were employed. Eventually, Red Al, $[(CH_3OCH_2CH_2O)_2AlH_2]Na$, was employed as the source of hydride under dilute conditions (−20 °C) to provide the desired bisallene-bisalkyne in 70% yield. Presumably, the red Al first reacted with the hydroxyl groups in **11a** to give an intermediate in a rapid process. In a subsequent step, hydride was delivered intramolecularly to the sp carbon atom adjacent to the hydroxyl group through a five-membered-ring transition state in an SN_2' fashion. This process furnished the desired allene **12** and was presumably the rate-determining step. A similar regioselectivity was reported in the reductive opening of an epoxy alcohol.[36] It is noteworthy that dilute conditions were found to be optimal. At high concentrations of hydride, the nucleophile attacked the propargylic carbon atom in an SN_2 displacement of chloride to diminish the yield of allene **12**. It was also important to note that a different batch of Red Al would occasionally result in a lower yield (~40%) of **12**. If the process was maintained at low temperature (< −10 °C), then the byproducts isolated were monoallene and the starting **11a**, which could be recycled to produce more of the desired bisallene **12**, if necessary. If one considers that two allenes were formed in the same one-pot process, then this was considered a pivotal reaction in this sequence. This was the first time, to these authors' knowledge, that Red Al was successfully employed for this transformation.[13]

Attempts to cyclize the bisallene-bisalkyne **12** under the reported conditions were carried out.[28] However, when **12** was heated in toluene in the presence of 2.4 equivalents of $Mo(CO)_6$ and 10 equiv of DMSO, analysis of the process indicated an inseparable mixture of products. This was not unexpected since similar results had been observed by Van Ornum in a different system.[24] On the basis of previous results, it was felt the free hydroxyl groups in **12** were not compatible with the conditions of the tandem Pauson−Khand reaction. The vicinal diol in **12** would require protection to constrain the geometry to promote the desired cyclization and this would remove the interference by the hydroxyl groups in the process as well.

A number of protecting groups were evaluated. As shown in Scheme 3, the bisallene-bisalkyne diol **12** was heated to reflux with excess 2,2′-dimethoxypropane in chloroform in the presence of a catalytic amount of anhydrous *p*TSA[24] (condition a, Scheme 3) to provide the desired acetonide **13**, albeit in low yield (30%-40%). The para-methoxybenzylidene acetal **14** could be formed more rapidly (4−5 h) by heating **12** with excess 4-methoxybenzaldehyde dimethyl acetal under the above condi-

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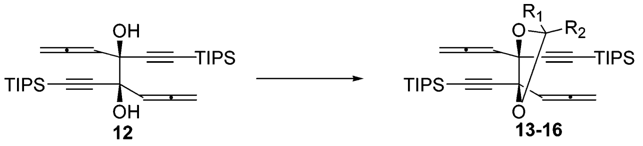
Scheme 3

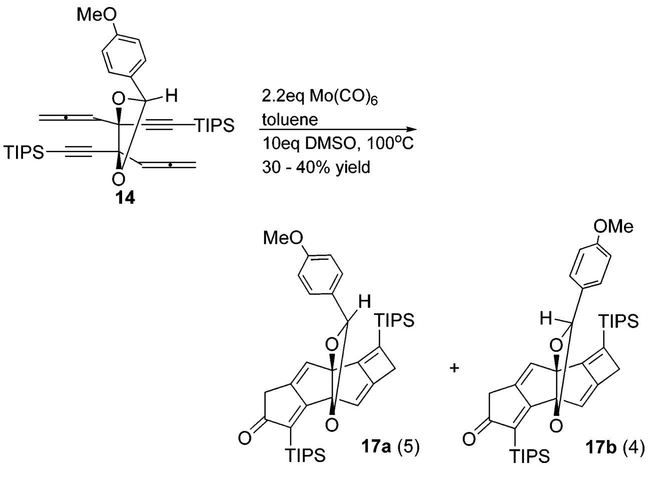


a, **13** ($R_1 = R_2 = Me$), excess $CMe_2(OMe)_2$, PTSA (anhydrous), reflux in toluene, 2 days, 38%.
b, **14** ($R_1 = H$; $R_2 = PhOMe$), excess $(MeO)_2CHPhOMe$, PTSA (anhydrous), reflux in $CHCl_3$, 4 hours, 91%.
c, **15** ($R_1 = H$; $R_2 = Ph$), excess $(MeO)_2CHPh$, PTSA (anhydrous), reflux in $CHCl_3$, 1 day, 60%.
d, **16** ($R_1 = H$; $R_2 = OEt$), excess $CH(OEt)_3$, CSA, CH_2Cl_2 (concentrated solution), 1 day , 70%.

tions in greater than 90% yield (condition b). Similarly, if benzaldehyde dimethyl acetal was employed under these conditions, the benzylidene acetal **15** was formed; however, this process required longer reaction times (24 h) and provided the acetonide **15** in lower yield (60%, condition c, Scheme 3). In addition, the cyclic ortho ester acetal **16** was also prepared (Scheme 3, condition d). This process required a high concentration of reagents (1 g of **12** in 2−3 mL of dry CH_2Cl_2). Under these conditions, the diol **12** was stirred with excess triethyl orthoformate in the presence of a catalytic amount of camphor sulfonic acid[32] to provide the ortho ester **25** in 70% yield (condition d).

Since the para-methoxybenzylidene acetal **14** was formed faster and in the highest yield, it was initially employed to explore the allenic tandem Pauson−Khand cyclization. Analogous to the conditions reported by Jeong[37] and Brummond et al.[28] the bisallene **14** was heated in toluene to 100 °C in the presence of a slight excess of Mo(CO)$_6$ (2.2 equiv) and 10 equiv of DMSO (Scheme 4). The reaction progress was monitored by TLC. In approximately 5 h, the starting **14** had been consumed and a new component of higher polarity was observed. The new component was isolated in approximately 40% yield and eventually found to be a mixture of diastereomers composed of the interesting [5.5.5.4] tetracycles **17a** and **17b** in a ratio of 5:4 (**17a**:**17b**). The structures of these tetracycles were elucidated by analysis of 2D NMR spectroscopy and one of these diastereomers (**17a)** was confirmed via X-ray crystallography. When the related bisallene−bisalkynes **15** and **16** were treated under the same conditions, similar tetracycles were isolated in similar yields.[29]

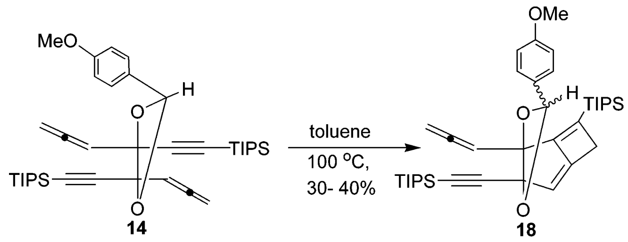
Scheme 4



The formation of the four-membered ring systems in **17a,b** under such conditions was intriguing. Recently, a similar phenomenon was reported by Shen and Hammond.[38] In that case, a terminal gem-difluoroallene was heated under the same conditions as described by Brummond et al.[28] to generate a four-membered ring in 80% yield. The quantity of Mo(CO)$_6$ could be reduced in that report to a catalytic amount (10%). The authors proposed the formation of this four-membered product resulted from reductive elimination of the corresponding molybdenum metallocycle rather than CO insertion. They reported that Mo(CO)$_6$ was required to provide the four-membered ring in that case.

In our hands, when the benzylidene acetal **14** was heated to 100 °C in the absence of Mo(CO)$_6$ and DMSO for a few hours, this provided a monocyclized four-membered ring bicycle **18** in 30 to 40% yield (Scheme 5). Consequently, in this case, the formation of the four-membered ring was not mediated by Mo(CO)$_6$. This was a thermally mediated [2+2] process (further evidence in support of this thermally mediated process can be found in the Supporting Information). This was an unusual reaction since most of the [2+2] cycloadditions of olefins are thermally forbidden. It has been suggested by a reviewer this might occur by a $\pi_{2a} + \pi_{2s}$ cycloaddition process, similar to that which has been reported in the case of ketenes with alkenes,[39,40] although, this thermal process involving an allene in place of a ketene is very rare. Tentatively, it is felt the rigid geometry of acetal **14** facilitated this intramolecular process (for more evidence see the Supporting Information); presumably, the orbitals involved were held in the preferred position in the acetal **14**. Upon heating to 100 °C, bond formation took place to provide **18**.

Scheme 5



It was clear that the reaction conditions would have to be finely tuned to provide the desired [5.5.5.5] tetracycles. Finally, on the basis of an understanding of the reaction mechanism,[29] modified reaction conditions were developed, which provided the desired [5.5.5.5] tetracycle **19** (68%) (condition a, Scheme 6). In this modification, a large excess of Mo(CO)$_6$ was heated in toluene to form a saturated solution. The best temperature for this cycloaddition process had been narrowed to the 53 °C to 55 °C range. The saturated Mo(CO)$_6$ solution certainly provided a higher concentration of the Mo−alkyne complex, to promote the tandem Pauson−Khand reaction at the expense of the thermal [2+2] process. Again, the narrow temperature range (53 to 55 °C) was important to obtain the [5.5.5.5] system

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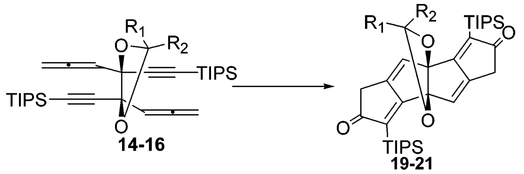
(40) The authors would like thank a reviewer for pointing this out.

Scheme 6



14 and **19** (R_1 = H; R_2 = PhOMe)
15 and **20** (R_1 = H; R_2 = Ph)
16 and **21** (R_1 = H; R_2 = OEt)

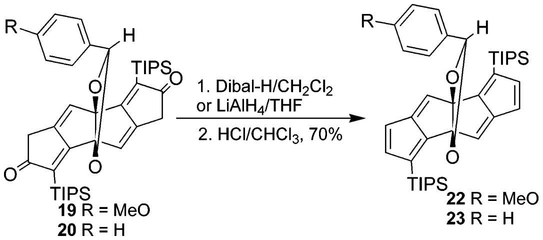
Conditions: a. Ar atmosphere, 10eq $Mo(CO)_6$/10eq DMSO/toluene, 53-55°C, 1 to 2 days; 65-70% yield.

b. CO atmosphere, 3 or 10eq $Mo(CO)_6$/10eq DMSO/toluene, 50 - 55°C; 1 day, no reaction.

in tetracycle **19**, and suppress the thermally mediated [2+2] process. A lower temperature retarded the reaction rate, while higher temperatures effected more of the undesired [2+2] four-membered ring formation in **17a** and **17b**. Under condition a, formation of the undesired **17a** and **17b** was suppressed to less than 10% of the reaction mixture. A suitable crystal was obtained from hexanes at low temperature (−30°), and an X-ray crystal structure of the [5.5.5.5] tetracycle **19** was obtained. If the Mo-mediated tandem allenic Pauson-Khand reaction was carried out under similar conditions with **15** and **16** (individually), then the corresponding tetracyclic systems (**20** and **21**) were obtained in similar yields (60−70%). It is important to point out each of the 6 new carbon−carbon bonds formed in this one-pot tandem sequence has occurred in 90−95% yield. It is noteworthy that in the presence of carbon monoxide (condition b, Scheme 6), only starting materials were detected and no new products were observed, while a large amount of $Mo(CO)_6$ still remained. These observations indicated the dissociation of the CO from $Mo(CO)_6$ was retarded by the presence of the CO, which retarded generation of a required vacant coordination site and the reaction as well.

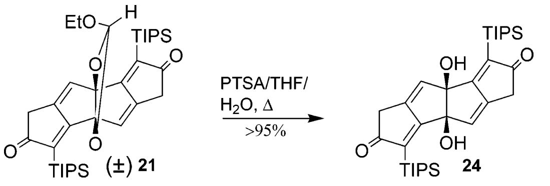
By study and modification of the two cycloaddition processes, the desired tetracyclic diketo tetraenes **19** to **21** could be prepared on gram scale (Scheme 6, condition a). The carbonyl groups in **19** and **20** were then reduced (individually) to provide a mixture of alcohols, respectively, on treatment with either Dibal-H or $LiAlH_4$ (Scheme 7). Both carbonyl groups in dione **19** or **20** were inert to $NaBH_4$. Although the epimeric alcohols from each dione could be separated by column chromatography, the crude mixture of diols was simply stirred in HCl (catalytic)/$CHCl_3$ to provide the bisfulvenes **22** and **23** (individually). Loss of both epimeric alcohol moieties provided the same hexaene. Both hexaenes **22** and **23** were prepared in individual experiments and isolated as orange-colored solids. This is a color typical of fulvenes.[1] These two triisopropylsilyl substituted fulvenes **22** and **23** were very stable under ambient conditions. Obviously, the huge triisopropylsilyl groups stabilized these molecules and prevented [4 + 2] cycloaddition side reactions from occurring. The fulvenes are regarded as polyenes and not aromatic molecules.[41] Attempts to eliminate the protecting groups in **22** and **23** to directly furnish the 14 π system in **1** all met with failure.[29]

Scheme 7



It was clear that milder conditions would be required to remove the two oxygen functions from **19** or **20** to provide the desired olefin functionality in the 14 π system. Attention turned to removal of the protecting group to regenerate the vicinal diol. It was known removal of the acetonide, para-methoxybenzylidene acetal or benzylidene acetal from the corresponding tetracyclic systems **19** and **20**, respectively, under mild conditions would be difficult, especially in the presence of the olefinic functionality. For this reason, the cyclic ortho ester acetal **21** was chosen for further study, since it would be easier to remove. Indeed, after a few attempts this protecting group was removed from dione **21** under mild conditions and in very high yield. As shown in Scheme 8, the cyclic ortho ester **21** was heated in aqueous THF (THF:H_2O = 20:1 v/v) to a gentle reflux to provide the desired tetracyclic diol **24** in very high yield (> 95%).

Scheme 8



Numerous methods were evaluated to remove the vicinal diol to generate the double bond.[29] Eventually, the vicinal diol in **24** was converted into an aminoacetal **25**, as shown in Scheme 9. The vicinal diol **24** was stirred with excess *N*,*N*-dimethylformamide dimethyl acetal in CH_2Cl_2 at room temperature to provide the tetracyclic aminoacetal **25** in 70% yield. This aminoacetal moiety in **25** was labile and was easily hydrolyzed by moisture. A few conditions were attempted to eliminate the aminoacetal moiety to form the double bond. Finally, the conditions developed by N−C. Yang et al.[42] proved successful.

The tetracyclic aminoacetal **25** was heated in toluene at 50 °C in the presence of diisopropylethylamine and trifluoromethane sulfonic anhydride (Scheme 9). A red-purple colored

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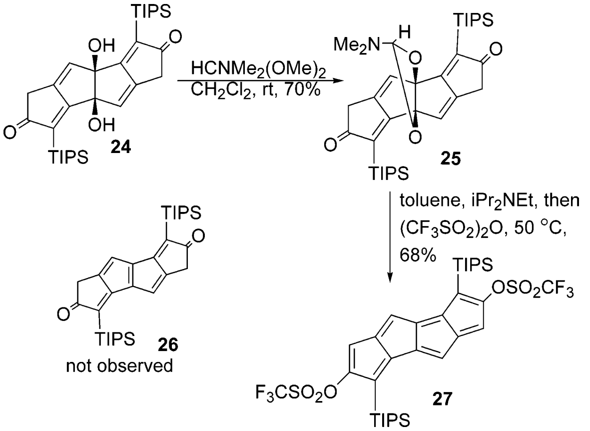
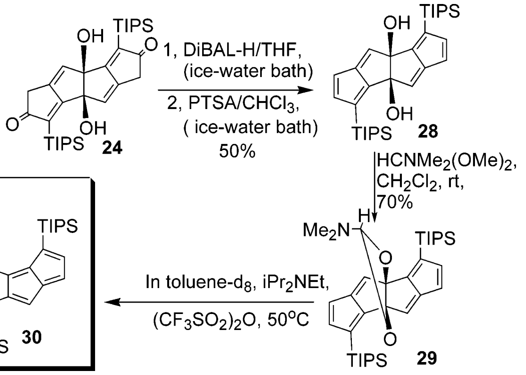
(41) Lewis, D.; Peters, D. *Facts and Theories of Aromaticity*; The Macmillan Press Ltd: London, 1975 1−61.

(42) King, J. L.; Posner, B. A.; Mak, K. T.; Yang, N.-C. *Tetrahedron Lett.* **1987**, *28*, 3919−3922.

Scheme 9



Scheme 10



material of low polarity was observed on TLC and isolated. It was assigned the structure of a 14 π system, a bisenol triflate **27,** based on spectroscopic studies. It appeared the desired elimination process had occurred, and the ketone functions had reacted with trifluoromethane sulfonic anhydride to produce the bisenol triflate.[43] Analysis of the ^{13}CNMR ($CDCl_3$) spectrum of this colored solid indicated the presence of seven signals in the area between δ 100 ppm to 171 ppm. This indicated **27** was a symmetrical molecule. The ^{1}HNMR ($CDCl_3$) spectrum of 14π system **27** contained two singlets at δ 7.76 and 6.95 ppm, which suggested some electronic delocalization. Attempts to prepare the intermediate dione **26** met with failure, moreover it had been reported the elimination step (formation of the double bond) in some systems could proceed slightly more readily than the enolization process.[42] When the amount of trifluoromethane sulfonic anhydride was decreased to less than 1 equiv and the process repeated with **25** at room temperature, only 14 π cross linked annulene **27** was observed, accompanied by consumption of the aminoacetal **25**. This result indicated the formation of the enol triflates occurred right after the elimination reaction took place. This formation of the 14 π cross linked annulene strongly suggested the energy barrier between diketone **26** and the 14 π system **27** was small. Apparently, there was a strong demand in dione **26** to be delocalized (enolized) to provide a 14 π cross linked annulene. This dicyclopentapentalene **27** was obtained as a red-purple colored solid, stable when kept at low temperature. Suitable crystals were grown, and the X-ray crystal structure was obtained (see below).

The synthesis of the disubstituted 14 π cross linked annulene was then explored. As shown in Scheme 10, the two carbonyl functions in diol **24**, presumably, could be converted into the corresponding olefins contained in the bisfulvene diol **28**. The reduction of the two carbonyl functions in **24** would provide a mixture of secondary alcohols which must undergo dehydration to provide the additional two double bonds in hexaene **28**. This might be achieved in the presence of the two bridgehead allylic tertiary alcohols under acidic conditions if the process were mild enough. Analysis of the geometry of either bridgehead diol bond in **24** or **28** by molecular models indicated these two molecules contained a rigid, bent geometry along the central carbon−carbon bond, which would render formation of carbocations at these tertiary positions a high-energy process. The bent geometry of such a system would prevent the developing p orbital of a potential carbocation from overlapping with the olefinic system and also prevent the sp^2 planar geometry required for carbocation formation. The acid-catalyzed removal of the corresponding, secondary alcohols in the presence of the tertiary alcohols was deemed a feasible process.

Consequently, the carbonyl functions in diol **24** were reduced to the corresponding alcohols by reaction with Dibal-H or $LiAlH_4$ (Scheme 10). The crude mixture of alcohols was then stirred under slightly acidic conditions at low temperature (ice water bath) for a short period of time to provide the yellow-gold colored bisfulvene diol **28** via an elimination process in a yield of 50%. The acidity, the temperature and the reaction time of this process must be carefully controlled. The proton NMR spectrum of this gold-colored bisfulvene diol **28** is shown in Table 1. The ring-proton signals appeared at 6.15, 6.65, and 6.77 ppm, respectively, which were very similar in chemical shift to those found in the dimer of pentalene reported by Hafner et al.[44] The hexaene **28** was obtained as a typical fulvene with an orange color, as mentioned earlier.

In comparison to the protected bisfulvenes (e.g., **22** and **23**), the hexaene diol **28** was much less stable, consequently it was immediately converted into the aminoacetal **29** when stirred with *N*,*N*-dimethylformamide dimethyl acetal (Scheme 10). In brief, treatment of the aminoacetal **29** with diisopropyl ethylamine and trifluoromethane sulfonic anhydride in toluene-d_8 at 50 °C provided a purple-colored material of low polarity (R_f, 0.95, hexanes, silica gel). On the basis of analysis by spectroscopy, this material was assigned the structure of the desired 14 π cross linked annulene **30**.[13] To date, this 14 π cross linked annulene **30** has survived only in solution: upon removal of the solvent under vacuum and in the presence of argon, a brownish-colored polymeric material was generated. This material could not be redissolved in nonpolar solvents.

Results and Discussion

X-ray Structural Analysis, UV/Visible Spectroscopy and NMR Spectroscopy of Hexaene 28, 14 π Cross Linked Annulenes 27, 30 and Related Compounds. As mentioned, slow evaporation of a solution of 14 π annulene **27** in hexanes furnished red-purple colored crystals of the bis triflate that were suitable for X-ray crystallography. Two views of the ORTEP drawing of this molecule **27** are illustrated in Figures 3 and 4. The X-ray structure of **27** in Figure 3 confirmed the structure of **27** as assigned via the NMR studies.[29] In addition, in Figure

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(43) Stang, P. J.; Treptow, W. *Synthesis* **1980**, 283−284.

(44) Hafner, K.; Dönges, R.; Goedecke, E.; Kaiser, R. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 337−338.

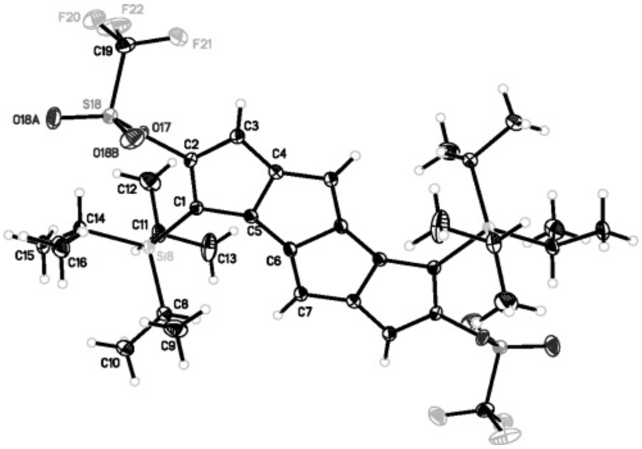


Figure 3. ORTEP drawing of the enol triflate **27**.

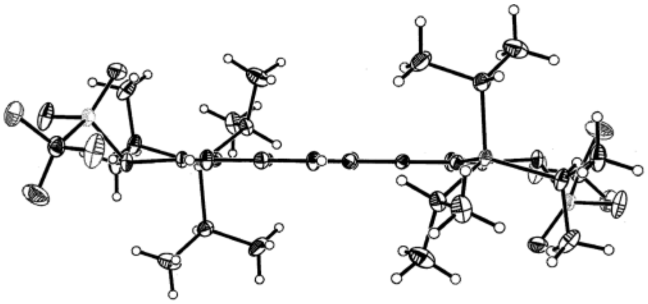
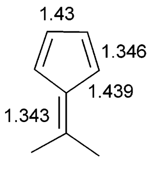


Figure 4. Planar 14 π system. The orthogonal view of the enol triflate ester **27**.

4, an orthogonal view of the X-ray structure of **27** is shown. It is clear the parent [5.5.5.5] system in cross linked annulene **27** is planar from this view. This indicated the fourteen sp^2 carbon atoms in **27** are in the same plane, accompanied by the appropriate delocalization.

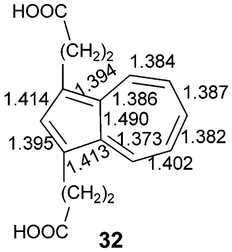
Most significantly, the bond lengths of the 14 π system **27** were now available, which are depicted in Figure 5 (for more data, see the Supporting Information). One of the criteria for aromatic delocalization is a measure of bond lengths. Benzene is a model aromatic system which contains uniform bond lengths of 1.395 Å in this Hückel 6 π delocalized system.[41] In aromatic annulenes, the bond lengths should approach 1.395 Å, according to the definition of aromaticity that had been earlier proposed.[41] The molecule would be classified as aromatic if the carbon–carbon bond lengths were between 1.36 and 1.43 Å in length, while the molecule would be termed a polyene if it contained alternating bond lengths of 1.34 to 1.356 Å for the double bonds (the length of a normal sp^2–sp^2 carbon–carbon double bond is 1.32 Å[45]) and 1.44 to 1.475 Å for the single bonds (the length of a normal sp^2–sp^2 carbon–carbon single bond is 1.48 Å).[45]

As shown in Figure 5, the 1,1′-dimethyl fulvene **31** is classified as an alternate olefin,[41] when this definition is applied. The bond lengths fit the criteria for a polyene. In the other example in Figure 5, it is known the 1,3-disubstituted azulene **32** is an aromatic molecule.[1,41] The bond lengths on the periphery of the ring are between 1.38 and 1.42 Å, which satisfy the criteria for an aromatic compound. The bridged single bond (1.49 Å) is longer than the bonds on the periphery, and is even longer than a regular sp^2–sp^2 carbon–carbon single bond (1.48 Å). This central bond is clearly not part of the conjugated system, indicative of the resonance delocalization on the periphery.[41] This molecule **32** can be represented more clearly as a simple aromatic 10 π cross linked annulene.[41]



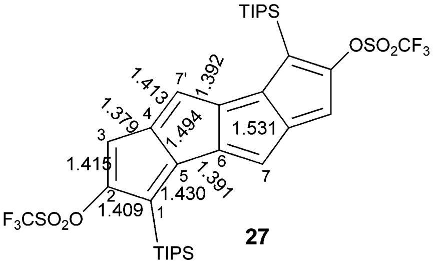
31

1,1'-dimethylfulvene



32

1,3-disubstituted azulene



27

Figure 5. Bond lengths of fulvene **31**, azulene **32** and 14π cross linked annulene **27**.

In the case of bisenol triflate 14 π cross linked annulene **27**, the bond lengths are much closer to the azulene than to the fulvene. Cross-linked annulene **27** is a symmetrical molecule, therefore, only half of the bond lengths are presented in Figure 5. Although the bond lengths on the periphery of **27** were not uniform and close to 1.395 Å (the length of those in benzene), they were similar to those in the azulene (Figure 5). The bond lengths on the periphery of **27** were between 1.38 Å to 1.43 Å. This fits the criteria for an aromatic compound,[41] even though the bond length of C(1)–C(5) (1.430 Å) reached the maximum limit for the definition. The two bridging carbon–carbon bonds in **27** were longer than the other bonds on the periphery, 1.4937 Å [C(4)–C(5)] and 1.531 Å [C(6)–C(6)′], respectively, in complete agreement with that observed for the aromatic azulene (Figure 5). Obviously, these two bridged bonds were not involved in the conjugated π system.

On the basis of the data on bisenol triflate **27** from X-ray crystallography and proton NMR chemical shifts (see below), it is proposed that **27** exhibited aromatic delocalization. The delocalization of the 14 π electrons in **27** may be less than that of azulene or benzene, but certainly **27** cannot be considered as an alternate cyclic polyene. As pointed out by a reviewer, polycyclic nonbenzonoid aromatic compounds that contain both [4*n*+2] cycles of electrons and [4n] cycles constitute an interesting family of molecules; the perimeter of annulene **27** contains 14 π electrons, but the skeleton contains pentalene subunits (8 π electrons). These types of molecules usually adjust their geometries in such a way as to maximize electron delocalization around the [4*n*+2] cycles while simultaneously minimizing the electron delocalization around the [4*n*] cycles. It is important to recognize the length of the central transannular C–C bond is 1.531 Å (Figure 5) in **27** instead of a bond length close to 1.48 Å expected for the C–C bond between two sp^2 carbon atoms (i.e., the 2–3 bond in butadiene). The molecule has

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(45) March, J. *Advanced Organic Chemistry*, 4th ed.; John Wiley and Sons: New York, 1992, 31–32.

Table 1. Assignment of the Proton and Carbon-13 NMR Signals of Targets **28**, **29** and **30**

	28 in $CDCl_3$, δ, ppm		**29** in $CDCl_3$, δ, ppm		**30** in C_6D_{12}, δ, ppm	
	proton	C-13	proton	C-13	proton	C-13
1 & 5	6.15	115.13	6.10, 6.20	115.10, 115.17	6.60	114.18
2 & 6	6.77	148.15	6.79, 6.86	147.87, 148.73	7.73	158.81
3 & 7		132.04		132.00, 132.56		122.60
4 & 8	6.65	136.51	6.63, 6.67	132.98, 133.08	7.32	118.97
9 & 12		151.64		151.51, 151.54		165.71
10& 13		154.28		153.97, 155.50		147.77
11 & 14		93.25		100.00, 100.60		148.32
OH	2.95					
$HC-NMe_2$			5.55, 2.63	116.72, 36.97		
TIPS	1.11, 1.29	11.7, 11.90	1.14, 1.38	11.70, 19.00	1.17, 1.51	13.12, 19.13

stretched the transannular bond almost to the length of the C−C bond in ethane. As a consequence, it has greatly diminished the π-bonding between these two carbon atoms and thereby minimized the unfavorable thermodynamic consequences of electron delocalization around the two pentalene subunits (i.e., the AB ring pair and the CD ring pair; note that the BC ring pair cannot be viewed as a pentalene without leaving the A and D rings as odd electron π systems). This is an example of a molecule adapting the minimum energy geometry, where aromaticity vs antiaromaticity contribute in addition to strain considerations.[46]

The tetra-*tert*-butyl substituted dicyclopenta[a,e]pentalene (**34**, Figure 6) reported by Stowasser, Lindner, and Hafner[12,47] was isolated as a brownish-violet solid. A crystal structure of **34** was also obtained by Lindner.[48] From examination of the crystallographic data kindly provided by Professor Lindner, it is clear the 14 carbon atoms of **34** line on the same plane. The bond lengths of this tetra *tert*-butyl annulene **34** are, however, somewhat different from those in annulene **27**. The bond lengths of **34** all lie between 1.40 and 1.42 Å, except for one bond related to C4−C7 in **27**, (Figure 5). In **34**, this bond was 1.45 Å long, this is beyond the maximum limit of the criteria for an aromatic compound.[41] More interestingly, the two bridged bonds are 1.445 and 1.478 Å, respectively. They are shorter and more similar to regular sp^2-sp^2 single bonds. The structure of this novel tetra substituted planar 14 π annulene is different from that of 14 π annulene **27**, but is completely consistent with results reported from this laboratory[12] by NMR spectroscopy (Figure 6).[12,47,48,53]

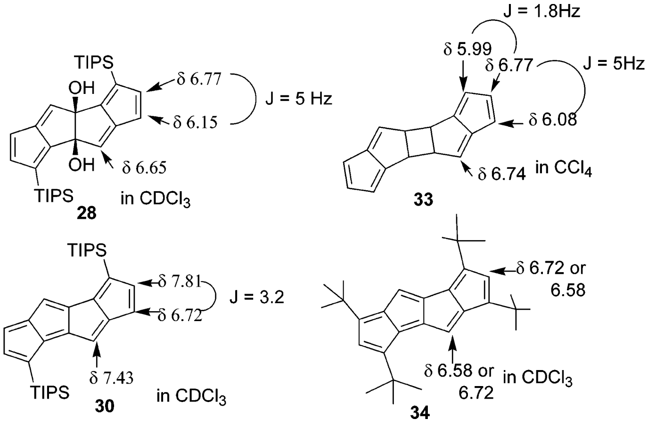

Figure 6. Proton NMR comparison of **30** and related compounds.

The UV spectra of bisfulvene diol **28**, the 14 π enol triflate **27** and the 14 π cross linked annulene **30** are illustrated in the Supporting Information. The maximum absorbance of these three materials appeared at 286 nm (**28**), 363 nm (**27**) and 354 nm (**30**), respectively. Obviously, there was a significant red shift in going from **28** to **27** and from **28** to **30**, in support of the fully conjugated Hückel 14 π systems in **27** and **30**. The similarity between the UV spectrum of **27** and **30** also supported a planar delocalized structure for cross linked annulene **30** in agreement with the results of NMR spectroscopy. Since the X-ray structure of **27** had been obtained, this lent support to the planar nature of **30** as well as **27**. The maximum absorbance of bis triflate **27** was further slightly red shifted (9 nm) in comparison to that of **30**. This was, presumably, due to the contribution of the two triflate auxochromes in **27**. The UV spectrum of the Stowasser/Hafner annulene **34** contained a maximum absorbance at 349 nm, which was slightly blue shifted relative to the 14 π cross linked annulene **30** (5 nm). While the UV spectra of these three molecules (**27**, **30**, **34**) are similar; however, they carry different substituents. As pointed out by a reviewer, these three molecules are nonbenzenoid compounds, the longest wavelength absorption of which could be abnormally sensitive to substituent effects, as demonstrated in the case of azulenes.[46,50] Although it appears **27** and **30** are more delocalized than **34**, these three molecules are the only members of this family that have been synthesized, and it is difficult to make unequivocal comparisons. One cannot exclude the possibility that the UV spectra of **27**, **30** and **34** fortuitously resemble each other and UV spectroscopy may not be a good measure of delocalization here.

The ^1H NMR and ^{13}C NMR spectra of **28**, **29** and **30** were assigned via extensive NMR studies of the 1D, 2D COSY, HSQC, HMBC, and NOESY spectra and are documented in Table 1. In 14 π cross linked annulene **30**, the two doublets in C_6D_{12} at $\delta = 6.60$ (d, $J = 3.2$ Hz) and 7.73 (d, $J = 3.2$ Hz) are due to signals from protons 1 (5) and 2 (6). The signal at $\delta = 7.32$ appeared as a singlet, consequently, it was assigned as proton 4 (8). The signal at $\delta = 6.60$ experienced a strong noe with the proton at $\delta = 7.73$ and a weak noe with the proton at $\delta = 7.32$, consequently, this signal could be assigned as proton 1 and the symmetrical 5 (Table 1). The nine signals in the carbon spectrum of **30** were in complete agreement with the structure of this target 14 π system.

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(46) The authors thank a reviewer for a detailed discussion of such phenomenon.

(47) Stowasser, B., Ph.D. Thesis; der Technischen Hochschule Darmstadt: Darmstadt, 1988.

(48) Lindner, H. J. Unpublished results, personal communication.

(49) It was point out by a reviewer that the X-ray structure of **34** could lie on a crystallographic center of inversion, a distinction between a delocalized structure of C_{2h}-symmetry and a superposition of two localized structures of C_s-symmetry is impossible.

(50) Gordon, M. *Chem. Rev.* **1952**, *50*, 127−199.

(51) Yoder, J., C.; Day, M. W.; Bercaw, J. E. *Organometallics* **1998**, *17*, 4946.

(52) Hafner, K.; Süss, H. U. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 575−576.

(53) Süss, H. U. Unpublished results, personal communication.

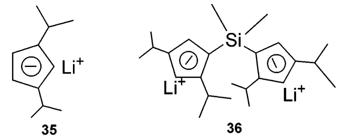
The comparison of the proton signals in the NMR spectra of **28**, **29** and **30** in $CDCl_3$ clearly indicated the protons on the periphery of 14 π cross linked annulene **30** are deshielded with respect to the corresponding signals in bisfulvenes **28** and **29**. For instance, in the bisfulvene diol **28**, the proton signals appeared at $\delta = 6.15$ (d, $J = 5$ Hz), 6.65 (s), and 6.77 (d, $J = 5$ Hz). While in 14π cross linked annulene **30**, the corresponding signals were located at $\delta = 6.72$ (d, $J = 3.2$ Hz), 7.43 (s), and 7.81 (d, $J = 3.2$ Hz) ppm, respectively, in $CDCl_3$. This constituted a marked difference of 0.57 ppm, 0.78 ppm and 1.04 ppm, respectively, between these signals in hexaene **28** and those in heptaene **30**. Finally, the spectrum of bisenol ester **27** contained signals for the ring-protons singles at 7.76 ppm(2H, s), and 6.95 ppm (2H, s). In agreement with the UV spectrosopy, the NMR studies also indicated that di-substituted **30** and tetra-substituted annulene **27** are similar in character.

The deshielding reflects electronic delocalization in 14 π cross linked annulene **30**.[41] The proton NMR spectrum of the tetra-*tert*-butyldicyclopenta[*a*,*e*]pentalene **34** (Figure 6) reported by Stowasser, Hafner et al., which was obtained as brownish-violet crystals, contained ring-proton signals at $\delta = 6.58$ and 6.72 (in $CDCl_3$).[12] Obviously, the signals of the 14π cross linked annulene **30** are downfield with respect to Stowasser/Hafner's material.[12,47] The largest difference is greater than 1 ppm (see protons 4 and 8, Figure 6). Clearly, the 14 π cross linked annulene **30** was more delocalized than the tetra *tert*-butyl cross linked annulene **34**. This is in agreement with a comparison of the bond lengths in the crystal structures of **27** and **34**[47,48] detailed previously, and the results of UV spectroscopy.

Since the delocalization in 14 π cross linked annulene **30** appeared to be different from that in planar annulene **34**, the effect of the two silyl substituents on the NMR chemical shifts in **30** must be taken into account.

Comparison of the chemical shifts of hexaene **28** to those of a similar compound, the dimer of pentalene **33**[44] (Figure 6), indicated the silyl substituents had almost no effect on the chemical shifts of the vinyl protons in **28**. The effects of the silyl substituents (TIPS) are almost negligible. Consequently, the TIPS groups do not affect the chemical shift differences observed between hexaene **28** and heptaene **30**. It is well-known that fulvenes are fixed alternate olefins;[41] compounds **28** and **33** clearly belong to this class. If the heptaene **30** were an alternate olefin, it would be reasonable to expect the substituent effect of the silyl group on the chemical shifts to be the same as observed in **28**, that is nearly negligible. However, there are large downfield shifts of the chemical signals of the protons on the periphery of **30** in comparison to those in **28** or **33**, and these arise from incorporation of the last double bond into heptaene **30**. This suggested a stronger delocalization in **30** as compared to **28** and **33** or even to the tetra *tert*-butyl cross linked annulene **34**.

There are limited cases in the literature which detail the substituent effect of the silyl and alkyl groups on the chemical shifts of a delocalized five-membered system. One example is depicted in Figure 7.[51] The difference between the proton chemical shifts of lithium 1,3-diisopropyl-cyclopentadienyide **35** and its silyl analogue **36** are about 0.3 ppm which are much smaller than the differences (0.8−1 ppm) observed between the 14π cross linked annulene **30** and the tetra *tert*-butyl cross linked annulene **34** prepared by Stowasser.[12,47] In addition, the chemical shifts of the ring protons of 1,3,5-tri-*tert*-butylpentalene, obtained by Süss[52] appeared at δ 5.07 ppm (4-H, 6-H) and 4.72 (2-H), respectively, while those of the related 1,3-di-*tert*-butyl-5-trimethylsilylpentalene appeared at 5.40 ppm (4-H, 6-H) and 4.85 (2-H).[53] Clearly, the difference in the effect of the trimethylsilyl group versus the *tert*-butyl group on the proton chemical shifts in the same polyquinene are very small.[52]



35 **36**

δ 5.37 ppm(1H), 5.33 ppm(2H) δ 5.67 ppm (1H), 5.62 ppm (1H)

Figure 7. NMR signals of the representative anions of substituted cyclopentadienes.

The chemical shifts of monosubstituted benzenes have been well documented. The presence of a *tert*-butyl group will effect a slight change in the chemical shifts of ortho, meta and para protons (0.02, −0.08, and −0.21 ppm, respectively). The presence of a trimethysilyl substituent will effect the corresponding proton shifts about 0.22, −0.02, and −0.02 ppm, respectively.[54] Obviously, the effects are small, and do not influence the chemical shift differences between hexaene **28** and 14π cross linked annulene **30**, as well as the difference between **30** and Stowasser/Hafner's **34**.

Finally, importantly, the three-bond coupling constant in heptaene **30** was 3.2 Hz in relation to the 5 Hz coupling constant in hexaene **28**. This indicated a delocalization in the five-membered heptaene **30** [illustrated in Figure 8 are the ^{3}J values of the localized five-membered carbocyclic rings (top) and delocalized five-membered carbocyclic rings (bottom)].[41] This difference in J values was due to the change in bond length. The slightly longer double bonds which resulted after delocalization in **30** are responsible for the smaller ^{3}J value.

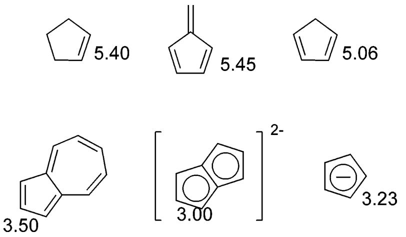


Figure 8. ^3J values of representative localized and delocalized five-membered carbocycles.[41]

On the basis of the NMR chemical shifts of heptaene **27** and **30** as well as the X-ray crystal structure of **27**, it is clear that 14 π cross linked annulenes **27** and **30** are delocalized when compared to hexaene **28**. In addition 14 π systems **27** and **30** undergo more delocalization than Hafner's tetra *tert*-butyl cross linked planar annulene **34** in agreement with the NMR studies and crystallography (see **27** vs **34**). The delocalization apparent in **30** vs **34** is a clear example that small changes in electron density in a conjugated ring system on substitution of different groups can change the properties of the molecule. In this case, annulene **30** appears to be more delocalized than expected when compared to the tetra *tert*-butyl analogue **34**.

Interestingly, as mentioned above, **30** can only survive in solution, even in the absence of air. The most reasonable ex-

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(54) Williams, D. H.; Fleming, I. In *Spectroscopic Methods in Organic Chemistry*; McGRAW−HILL: London, New York, 1995; p 9.

planation, to date, is the molecules of the disubstituted annulene **30** can approach each other much easier than those in the tetra *tert*-butyl analogue **34** of Stowasser/Hafner. Consequently, polymerization can take place, presumably via a radical process, more readily in the case of **30** in comparison to the more stable **34**. This is similar to that observed in tri-*tert*-butyl pentalene.[52]

Attempts to Trap the 14π Cross Linked Annulene 30 and its Desilylated Parent 1. The strong dienophiles maleic anhydride and *N*-phenyl maleimide were added (individually) into the solution of heptaene **30** in benzene. The solution which resulted was then heated to 50 °C for 3 h and analyzed by TLC. A new component was **not** observed. The solvent was removed to dryness by blowing argon into the solution. In 12 h, the reaction was checked again by TLC. The cross linked annulene **30** still was observed and no new component was found. It was believed the huge excess of maleimide protected/insulated the heptaene **30** from reaction with itself or with oxygen.

The reactive diene, 1,3-diphenyl-isobenzofuran was also employed under similar conditions. Only starting materials were observed. When the same trapping experiment was done and TBAF was added, the cross linked annulene **30** was consumed, but only baseline material and the 1,3-diphenyl-isobenzofuran were observed on TLC.

Removal of the triisopropylsilyl groups from heptaene **30** to generate the parent ring system **1** was also attempted. A THF-d_8 solution of heptaene **30** was placed in an NMR tube and an initial proton NMR spectrum was recorded. Solid TBAF was then added into the tube. Within a few seconds, a large amount of black precipitate formed. A proton NMR spectrum was taken again. The olefin signals of the ring protons of **30** had disappeared, while no significant new signals were observed except for the signals that belonged to TBAF and the TIPS groups.

Conclusions

Two 14 π cross-linked annulenes which belong to the family of dicyclopenta[*a*,*e*]pentalenes have been synthesized and studied spectroscopically as well as by X-ray structural analysis. These two molecules are the 14 π bis enol triflate ester **27** and the 3,7-diisopropylsilyl substituted 14 π cross linked annulene **30**. The new allenic tandem Pauson-Khand reaction mediated by $Mo(CO)_6$ was employed as the key reaction to build up the core of the tetracycles. The reaction conditions required modification from the original ones to fit this purpose. Since six carbon−carbon bonds were formed in this one-pot process, each bond formation has occurred in greater than 90−95% yield, respectively, depending on the tetracycle, so generated. A highly DL stereoselective (dl:meso = 6:1) approach to the desired bisalkene-bialkyne **11** was developed: zinc stabilized carbanions proved to be the best nucleophiles to provide the desired stereoselectivity. Red-Al was employed for the first time to convert the propargyl chloride functionality in **11a** into the allene **12**. In addition, a cyclic ortho ester (**16** and **21)** was successfully employed as a protecting group in the tandem Pauson−Khand reaction, since it could be easily introduced and removed under mild conditions. This was essential for the synthesis of **30** and extented the utility of the tandem Pauson−Khand reaction.

The two dicyclopenta[*a*,*e*]pentalenes **27** and **30** underwent significant electronic delocalization, perhaps even aromaticity, as revealed by the planar nature of the X-ray structure of **27**. The teracyclic rings in **27** assumed a flat geometry (Figure 4); the bond lengths of the tetracycle in **27** also fit well into the criteria for aromatic compounds. A comparison of the NMR and UV spectra of both **27** and **30** demonstrated that they both exhibited similar electronic properties, therefore, the purple colored 14 π cross linked annulene **30** was planar as well as delocalized. Although both **27** and **30** are more delocalized than **34** based on spectroscopy, the lesser stability of **30** versus **34**, stems from the disposition of the tetra *tert*-butyl groups in **34**. Dimerization (see **33**) or polymerization via radical processes or perhaps $\pi_{2a} + \pi_{2s}$ cyclizations[39] in **34** are retarded, but such stabilization is not present in annulene **30**.

Experimental Section

The ^{1}H NMR spectra were recorded on a Bruker 300-MHz or 500-MHz multiple-probe instrument. Infrared spectra were recorded on a Thermo Nicolet Nexus 870 FT−IR E. S. P. spectrometer or a Perkin-Elmer 1600 Series FT−IR spectrometer. Low resolution mass spectral data (EI/CI) were obtained on a Hewlett-Packard 5985B gas chromatography−mass spectrometer. Microanalyses were performed on a CE Elantech EA 1110 elemental analyzer. UV spectra were taken on a Hewlett-Packard 8453 UV−vis spectrophotometer.

Analytical TLC plates employed were E. Merck Brinkman UV active silica gel (Kieselgel 60 F254) on plastic while silica gel 60A, grade 60 for flash and gravity chromatography, were purchased from E. M. Science.

Most chemicals were purchased from Aldrich Chemical Co. and were used without further purification, unless otherwise noted. Molybdenum hexacarbonyl was purchased from Strem Chemical Company.

Modified Procedure for the Molybdenum Hexacarbonyl Mediated Allenic Pauson−Khand Reaction to Form the [5.5.5.5] Tetracycles 19, 20, and 21 at 55 °C. A mixture of $Mo(CO)_6$ (6.3 g, 24 mmol) in toluene (120 mL) was heated to 50 °C for 2 h in order to form a saturated solution. The solution of the ortho ester **16** (1.35 g, 2.43 mmol) and DMSO (2.01 g, 26 mmol) in dry toluene (20 mL) was added into the mixture. The mixture which resulted was heated at 53 to 55 °C for 36 h and then was filtered to remove solids. The precipitate was washed with hexanes (2 × 20 mL). The combined organic layers were concentrated under reduced pressure. The residue was purified by gradient column chromatography (silica gel, hexanes to 5% EtOAc−hexanes) to afford tetraene **21 (**0.96 g, 66%). This tetracycle can be crystallized from hexanes.

21: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.18 (1H, s), 6.14 (1H, s), 5.96 (1H, s), 3.54 (2H, m), 2.95 (4H, m), 1.08 and 1.58 (total 45H, m and m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.15, 209.97, 182.26, 181.77, 150.48, 149.84, 138.83, 122.67, 122.03, 119.77, 99.10, 59.97, 36.28, 19.09, 14.77, 11.58; EIMS (*m*/*z*, relative intensity) 567 (15), 493 (100), 451 (50). IR (thin film) 1704 (s), 1462(m), 1079 (m) cm^{-1}.

Anal. Calcd. for $C_{35}H_{54}O_5Si_2$: C, 68.80%; H, 8.91%. Found: C, 68.67%; 8.93%.

The tetracyclic para-methoxybenzylidene acetal **19**, was synthesized from **14** in 70% yield under conditions analogous to those described above. An X-ray crystal structure was obtained for **19**.

19: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (1H, s), 7.32 (1H, s), 6.91 (1H, s), 6.88 (1H, s), 6.22 (1H, s), 6.18 (1H, s), 5.85 (1H, s), 3.87 (3H, s), 3.01 (4H, m), 1.12 and 1.58 (total 42H, m and m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.37, 160.68, 153.03, 150.29, 139.77, 139.30, 128.48, 127.24,121.88,121.18, 113.56, 106.02, 100.07, 55.25, 36.54, 19.15, 11.56, 210.29, 182.24, 181.47, CIMS (*m*/*z*, relative intensity) 630 (80), 566 (18), 537 (15), 493 (100).

Anal. Calcd. for $C_{40}H_{56}O_5Si_2$: C, 71.38%; H, 8.89%. Found: C, 71.78%; 8.77%.

The tetracyclic benzylidene acetal **20** was synthesized from **15** in 67% yield under the conditions analogous to those described above.

20: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (2H, m); 7.35 (3H, m), 6.24 (1H, s), 6.21 (1H, s), 5.88 (1H, s), 3.05 (4H, m), 1.10 and1.62 (total 42H, m and m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.13; 210.03, 181.92, 181.17, 152.96, 150.20, 139.70, 139.25, 134.94, 129.56, 128.06, 126.81, 121.67, 120.96, 113.56, 105.90, 100.13, 36.34, 19.06, 11.42; CIMS (*m*/*z*, relative intensity) 642 (15), 600 (21), 493 (100). IR (thin film) 1701 (s), 1638 (m), 1564 (m), 1074 (m).

Anal. Calcd. for $C_{39}H_{54}O_4Si_2$: C, 72.85%; H, 8.46%. Found: C, 73.00%; 8.74%.

Trifluoromethanesulfonic Acid 6-Trifluoromethanesulfonyloxy-3,7-bis-(triisopropyl-silanyl)-dicyclopenta[*a*,*e*]pentalen-2-yl Ester 27. The diol-diketone **24 (**100 mg, 0.18 mmol) was stirred with an excess of the *N*,*N*-dimethyl formamide dimethyl acetal (300 mg) in $CHCl_3$ (3 mL) for 3 h until analysis by TLC (silica gel) indicated the starting material had disappeared and a new spot of lower polarity appeared. The solvent and excess formamide dimethyl acetal were removed under reduced pressure. The crude product could be purified by flash column chromatography [alumina (basic), 5% EtOAc/hexanes] to provide the amino acetal **25**, or, as in most cases, used directly in the next step.

Tetracyclic Diketo Amino Acetal 25: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.16 (1H, s), 6.14 (1H, s), 5.52 (1H, s), 3.05−2.91 (4H, m), 2.34 (6H, s), 1.60 and 1.10 (total 42H, m and m).

^{13}C NMR (75 MHz, $CDCl_3$) δ 210.4 (2 C), 182.87, 181.94, 151.64, 149.72, 139.11, 138.78, 122.47, 122.38, 116.33, 97.59, 97.43, 36.76, 36.4 (2 C), 19.10, 11.55.

The resulting crude product was then dissolved in toluene (2 mL) and the diisopropyl ethylamine (0.20 mL) was added. After heating the solution to 50 °C (bath temperature), triflic anhydride (0.1 mL) was added via a syringe. The solution turned black immediately, and a large amount of black precipitate appeared. The mixture was stirred for an additional 10 min and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (silica gel: cyclohexane) to provide a red-purple colored solid **27** (49 mg, 0.063 mmol, 35% for two steps). The crystals of **27** were obtained by slow evaporation of the solvent (hexanes) that contained this solid at room temperature. An X-ray crystal structure of **27** was obtained using these purple-colored crystals (see Figures 4 and 5).

27: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (2H, s), 6.95 (2H, s), 1.15 & 1.73 (42H, m and m), ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.29, 161.96, 148.01, 142.13, 121.10, 111.41, 102.66, 18.65, 12.32; IR (thin film) 3349 (m), 1457 (m), 1073 (m), 882 (m) cm^{-1}; UV (cyclohexane) λ_{max}(logϵ): 362 (4.86), 560 (2.93), 542 (3.03), 586 (2.92).

3,7-Bis-(triisopropyl-silanyl)-dicyclopenta[*a*,*e*]pentalene-3b,7b-diol 28. A solution of diol **24** (120 mg, 0.21 mmol) in dry THF (15 mL) was cooled in an ice−water bath. DiBAL-H (1.5 mL, 1 M solution in toluene) was syringed into the solution at 0 °C. The solution was stirred for 2 h, after which it was quenched with an aq solution of NH_4Cl (5 mL). Ethyl ether (20 mL) was then added into the solution. The organic layer was separated and the aq layer was extracted with ether (3 × 10 mL). The combined organic layer was dried ($MgSO_4$) and the solvent was removed under reduced pressure. The crude product was dissolved in $CHCl_3$ (20 mL), after which the solution was cooled in an ice−water bath. The *p*TSA (15 mg) was then added into the solution. Approximately 10 min later, the yellow solution took on a green colored appearance, after which aq $NaHCO_3$ (1 N, 10 mL) was added. The aq layer was extracted with $CHCl_3$ (3 × 10 mL). The combined layer was dried ($MgSO_4$) and the solvent was removed under reduced pressure. The residue was purified by gradient flash column chromatography (silica gel, hexanes to 2% EtOAc/hexanes) to provide hexaene **28** (54 mg, 50% for the two steps). This yellow colored solid was unstable under ambient conditions, and was immediately converted into the amino acetal **29**.

28: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.77 (2H, d, J = 5 Hz), 6.65 (2H, s), 6.10 (2H, d, J = 5 Hz), 2.95 (2H, m), 1.11 & 1.29 (42H, m and m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.28, 151.64, 148.15, 136.51, 132.04, 115.13, 93.25, 19.06, 11.75; IR (thin film) 3349 (m), 1457 (m), 1073 (m), 882 (m) cm^{-1}; UV (cyclohexane) λ_{max}(logϵ): 286(4.92), 381(4.20).

This material was employed directly in the next step.

***N*,*N*-Dimethyl Amino Acetal of 1,7-Bis-(triisopropyl-silanyl)-dicyclopenta[*a*,*e*]-pentalene-3b,7b-diol (see 29).** To a solution of hexaene **28** (50 mg, 0.096 mmol) in CH_2Cl_2 (2 mL) was added the *N*,*N*-dimethyl formamide dimethyl acetal (300 mg). The solution which resulted was stirred for 3 h, after which the solvent was removed under reduced pressure. The reaction could also be performed by using the *N*,*N*-dimethyl formamide dimethyl acetal as the solvent. The acetal was purified by flash chromatography [alumina (basic), 2% EtOAc/hexanes] to provide **29** (38 mg, 70%). (**Note: silica gel effects the hydrolysis of the amino acetal group**). The crude product could also be dried under high vacuum for a few hours, and then employed directly in the next step.

29: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.86 (1H, d, J = 5 Hz), 6.79 (1H, d, J = 5 Hz), 6.67 (1H, s), 6.63 (1H, s), 6.20 (1H, d, J = 5 Hz), 6.10 (1H, d, J = 5.0 Hz), 5.55 (1H, s), 2.36 (6H, s), [1.14 (m), 1.38 (m) (total 42H)]; ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.50, 153.97, 151.54, 151.51, 148.73 (C−H), 147.87 (C−H), 133.08 (C−H), 132.98 (C−H), 132.56, 132.00, 116.72 (C−H), 115.17 (C−H), 115.10 (C−H), 100.60, 100.00, 36.97, 19.0, 11.70; IR (thin film) 1460 (m), 1058 (m), 1011 (w), 800 (w) cm^{-1}.

3,7-Bis(triisopropyl-silanyl)-dicyclopenta[*a*,*e*]pentalene 30. The solution of hexaene **29** (23 mg, 0.038 mmol) in toluene-d_8 (0.8 mL) was heated to about 50 °C. Diisopropyl ethylamine (0.027 mL, 0.152 mmol) was then syringed into the mixture, followed by the addition of trifluoromethane sulfonic anhydride (0.014 mL, 0.18 mmol). The dark colored solution that resulted was allowed to stir for 0.5 h. The mixture was purified by flash column chromatography (silica gel, cyclohexane). This column was packed and run under an atmosphere of argon. The solvent of the purple colored solution containing the desired heptaene **30** was then removed by blowing argon into the vessel. Just before the solvent had completely evaporated, cyclohexane-d_{12} (0.5 mL) was added and removed by the same process. Just before the vessel went dry again, the heptaene was dissolved in cyclohexane-d_{12}. The NMR spectra were initially taken directly by using this solution. Later, the NMR spectra were also taken in pure $CDCl_3$. Again, the solution was never allowed to go dry.

30: ^{1}H NMR (300 MHz, C_6D_{12}) δ 7.73 (2H, d, J = 3.2 Hz), 7.36 (2H, s), 6.60 (2H, d, J = 3.2 Hz), 1.17, 1.51 (42H, m and m); ^{13}C NMR (75 MHz, C_6D_{12}) δ 165.71, 158.81 (C−H), 148.29, 147.77, 122.60, 118.85 (C−H), 114.04 (C−H), 19.13, 13.12, UV (cyclohexane): λ_{max}(logϵ) 354 (ca. 4.38), 521 (ca. 2.95), 586, (ca. 2.65), 627 (ca. 2.30).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (2H, d, J = 3.2 Hz) 7.43 (2H, S), 6.72 (2H, d, J = 3.2 Hz), 1.16, 1.59 (42H, m and m). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.62, 158.4 (C−H), 148.51, 147.30, 122.81, 118.48 (C−H), 113.64 (C−H), 18.78, 12.18.

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Supporting Information Available: Experimental details and data for compounds **10**, **11a**, **11b**, **12**, **14**, **16**, **17a**, **17b**, **23**, **24** as well UV spectra for **27**, **28**, **30** and proton NMR spectra for **28**, **29**, and **30**. This material is available free of charge via the Internet at http://pubs.acs.org.

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