Hydrogen-protected acenes†

Andreas J. Athans, Jonathan B. Briggs, Wenling Jia and Glen P. Miller*

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The first systematic study concerning the hydrogenation of acenes and acene quinones is presented. Phenyl substituted acenes and acene quinones are hydrogenated in excellent yield and with complete regioselectivity using HI–AcOH. The resulting H-protected acenes bear alternating aromatic and non-aromatic rings and are stable, soluble molecules that may be stored indefinitely and then deprotected to afford the parent acenes. In this manner, H-protected acenes have been utilized in the syntheses of several [60]fullerene-acene adducts. Buckminsterfullerene also hydrogenates in HI–AcOH yielding C_{3v} symmetric $C_{60}H_{18}$.

Introduction

Large acenes with five or more rings are potentially useful components in organic light emitting diodes (OLEDs),[1] thin film transistors[2] and sensors,[3] among other electronic devices.[4] Moreover, large acenes represent interesting platforms on which to append fullerenes[5] *via* Diels–Alder cycloaddition reactions. Despite the fact that large acenes possess a growing number of both technological and chemical applications, their utility is limited by poor solubility and photo-instability.[6] While the poor solubility of large acenes may be remedied by preparing compounds with suitable substitution,[7] their photo-instabilities are more challenging obstacles to overcome. Acenes are believed to photosensitize singlet oxygen formation and then react with singlet oxygen in a [4 + 2] fashion. The mechanism of this reaction has been studied computationally and may change as a function of acene size.[8]

One approach to circumvent the instability of large acenes is to introduce stabilizing substituents. Payne *et al.* reported[9] the synthesis and characterization of a stabilized hexacene disubstituted with tri-*tert*-butylsilyl ethynyl substituents as well as a stabilized heptacene disubstituted with tris(tri-*tert*-butylsilyl)silyl ethynyl substituents. It was argued that the bulky nature of the tri-*tert*-butylsilyl and tris(tri-*tert*-butylsilyl)silyl groups afforded the acenes greater kinetic stability. While this steric effect is no doubt an important one, the electronic effect afforded by the ethynyl groups also contributes. We previously noted that 6,13-diphenylethynylpentacene shows greater stability in solution than 6,13-diphenylpentacene[10] and attributed this effect to electronic stabilization. That is, the enhanced electronegativity of the sp hybridized carbons on the ethynyl linkages renders the acene less dienophilic in Diels–Alder reactions with singlet oxygen. Likewise, we previously prepared and studied 6,13-bis(trimethylsilylethynyl)pentacene and attributed its reduced reactivity to a combination of steric and electronic factors.[11]

While the aforementioned ethynyl substituted acenes may be safely stored for relatively long durations in the solid state, they do nonetheless decompose in solution. Instability problems are especially pronounced for acenes larger than pentacene. In fact, there are few experimental reactivity studies associated with these large acenes. Reactivity studies of acenes larger than pentacene are typically theoretical in nature.[8,12]

Another approach to thwart acene instability is to prepare and manipulate protected acenes. An ideal protecting group for an acene is one that adds readily, imparts additional solubility, allows for long-term storage, and is deprotected under mild conditions. In this regard, Herwig and Müllen prepared several bridged pentacene adducts that were spin coated onto solid substrates and then heated to thermally extrude (retro-Diels–Alder reactions) the bridges (*e.g.*, ethylene or 1,2,3,4-tetrahalobenzene).[13] Under optimal conditions, the method produces ordered thin films of pentacene with high mobilities. However, the technique does not produce acenes in solution where they may be further manipulated. Moreover, the high temperatures required for the retro-Diels–Alder reactions (180–250 °C) render the method unsuitable for larger, less stable acenes.

More recently, Yamada *et al.* prepared a bridged α-dione precursor of pentacene and successfully converted it to pentacene in 74% yield *via* photolysis (photodecarbonylation) in toluene.[14] Mondal *et al.* extended this photochemical methodology to heptacene,[15] successfully preparing the large acene in a PMMA matrix where it persisted for several hours. The same photolysis reaction performed in solution did not produce isolable heptacene, but gave instead singlet oxygen adducts. The facile oxidation of heptacene in solution underscores the difficulties associated with reactivity studies of large acenes in solution.

Because we wish to study the solution phase chemistries of large acenes, we have considered the aforementioned and alternative acene protecting strategies including the simplest possible protecting group—hydrogen. Hydrogen protected acenes offer several key advantages: (1) hydrogenated acenes can be directly prepared from either the parent acene or, conveniently, a corresponding acene quinone; (2) hydrogenated acenes show vastly improved solubility compared to the parent acenes and acene quinones; (3) hydrogenated acenes are

Department of Chemistry, University of New Hampshire, Durham, NH 03824-3598, USA

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generally stable structures that can be stored for long durations without decomposition; (4) hydrogenated acenes may be deprotected (*i.e.*, dehydrogenated) using reagents like chloranil or 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ).[16] We report here our studies aimed at utilizing hydrogen as a simple, versatile protecting group for acenes. This effort represents the first systematic study of acene and acene quinone hydrogenations. In all cases, we utilized mixtures of HI and AcOH as reductant. Given our success in hydrogenating amines, we also attempted and now report the successful HI–AcOH reduction of [60]fullerene which produces C_{3v} symmetric $C_{60}H_{18}$ in excellent yields.

Experimental

Typical H-protection procedure

Approximately 100 mg of the acene or acene quinone reactant is loaded into a 250 mL round-bottomed flask along with 20–25 grams of aqueous HI (47% by weight) and 150 mL of glacial acetic acid. The mixture is heated to boiling for 5 days in the dark under nitrogen. Following the addition of saturated aqueous sodium bisulfite, the mixture is extracted with methylene chloride and washed successively with aqueous bisulfite, water and brine. The organic layer is dried with $CaCl_2$ and then concentrated under reduced pressure to give hydrogenated acene product. Further purification, if warranted, is achieved *via* silica column chromatography.

6,13-[60]Fulleren-6,13-dihydropentacene, 1

A mixture of hydrogenated pentacene compounds (50 mg, ~0.18 mmol) and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ, 310 mg, 1.37 mmol) is added to a solution of [60]fullerene (502 mg, 0.70 mmol) in toluene (150 ml). The resulting mixture is boiled for 2 days in the dark under nitrogen. The solution is concentrated under reduced pressure and washed with copious acetone. Compound **1** is separated from the crude product mixture by column chromatography (silica, CS_2 eluent). The first band corresponds to unreacted [60]fullerene and is followed by a second band that contains both **1** and [60]fullerene. Preparative thin-layer chromatography (silica, 1000 μm, CS_2 eluent) is utilized to isolate **1**. Yield of **1**: 87.8 mg (49.4%). FT-IR (KBr): ν/cm^{-1} 3048, 1731, 1605, 1514, 1462, 1427, 1262, 1186, 1181, 1092, 1019, 947, 879, 853, 809, 765, 745, 708, 702. ^{1}H NMR (360 MHz, CS_2–$CDCl_3$): δ 6.14 (s, 2H), 7.54 (m, 4H), 7.98 (m, 4H), 8.27 (s, 2H). ^{13}C NMR (90.56 MHz, CS_2–2% acetone-d_6): δ 58.1, 72.2, 124.7, 126.5, 128.3, 133.1, 137.1, 138.9, 140.0, 141.7, 142.1, 142.2, 142.6, 142.9, 143.1, 144.6, 145.40, 145.44, 145.6, 146.2, 146.4, 147.5, 155.4. MS (MALDI TOF): calcd: 998.1 (100%), 999.1 (89%) (M^+); found: 999 (M^+), 721 ($[C_{60}]^+$), 278 ([pentacene]$^+$).

6,13-[60]Fulleren-6,13-dihydro-5,7,12,14-tetraphenylpentacene, 2

A round-bottomed flask is charged with 5,7,12,14-tetraphenyl-6,13-dihydropentacene (79.2 mg, 0.135 mmol), [60]fullerene (490 mg, 0.68 mmol), DDQ (307 mg, 1.35 mmol) and 200 ml toluene. The solution is boiled in the dark for 2 days under nitrogen. The resulting solution is concentrated under reduced pressure and washed with copious acetone. Compound **2** is isolated by column chromatography (silica, CS_2 eluent). Yield of **2**: 99.3 mg (56.2%). ^{1}H NMR (360 MHz, $CDCl_3$): δ 5.91 (s, 2H), 6.99–7.03 (m, 4H), 7.19–7.24 (m, 4H), 7.34–7.40 (m, 12H), 7.40–7.46 (m, 4H), 7.53–7.58 (m, 4H). ^{13}C NMR (90.56 MHz, $CDCl_3$): δ 52.33, 71.58, 125.85, 127.06, 127.17, 128.02, 128.34, 130.16, 130.52, 132.17, 135.59, 136.13, 136.31, 137.23, 139.75, 141.60, 141.78, 141.88, 142.35, 142.90, 144.36, 145.12, 145.13, 145.16, 145.23, 145.94, 146.14, 147.25, 155.41.

cis,cis-5,18-[60]Fulleren-7,16-[60]fulleren-9,14-[60]fulleren-5,7,9,14,16,18-hexahydro-6,8,15,17-tetraphenylheptacene, 3

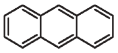
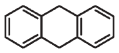
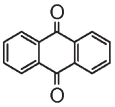
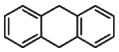
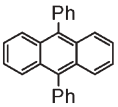
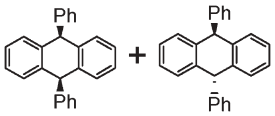
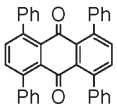
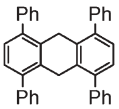
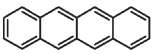
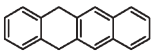
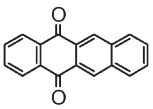
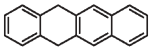
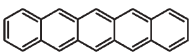
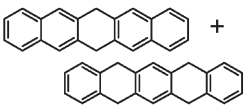
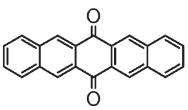
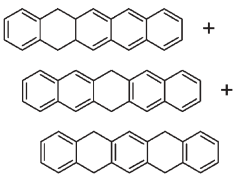
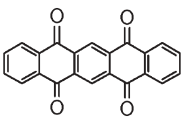
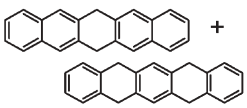
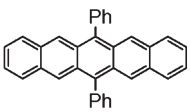
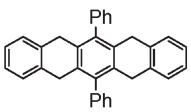
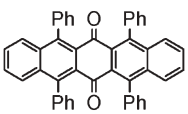
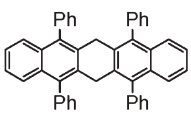
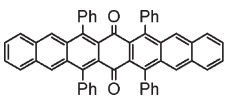
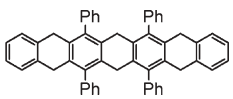
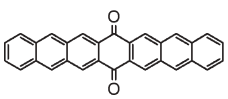
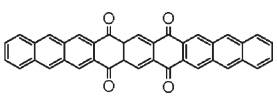
A nitrogen flushed round-bottomed flask is charged with 5,7,9,14,16,18-hexahydro-6,8,15,17-tetraphenylheptacene (40.9 mg, 5.9×10^{-5} mol), [60]fullerene (220 mg, 3.1×10^{-4} mol), and benzene (130 mL). To this solution is added DDQ (118.0 mg, 5.2×10^{-4} mol) in one portion. The mixture is boiled with stirring under N_2 in the dark for 20 hours. The benzene is concentrated under reduced pressure and the residue is washed with copious ethanol. Compound **3** is isolated by column chromatography (silica, CS_2). Yield of **3**: 33.8 mg (20%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.69 (s, 4H), 5.80 (s, 2H), 6.85 (d, 4H), 7.07 (t, 4H), 7.35 (t, 4H), 7.43 (m, 4H), 7.46 (d, 4H), 7.50 (t, 4H), 7.54 (m, 4H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 52.2, 55.1, 72.1, 72.5, 125.6, 127.2, 127.6, 128.2, 128.4, 128.7, 129.2, 129.9, 136.2, 136.6, 136.7, 136.9, 138.82, 138.84, 139.6, 139.79, 139.83, 141.4, 141.5, 141.6, 141.81, 141.82, 141.85, 141.88, 141.94, 142.32, 142.35, 142.40, 142.41, 142.44, 142.48, 142.54, 142.8, 144.42, 144.46, 144.50, 145.06, 145.10, 145.12, 145.18, 145.22, 145.44, 145.45, 145.95, 145.98, 146.00, 146.22, 146.26, 146.27, 147.30, 147.32, 155.0, 155.5. MS (MALDI TOF): *m/z* calcd: 2843.3 (79%), 2844.3 (100%), 2845.3 (84%) (M^+); *m/z* found: 683, 684 ($C_{54}H_{34}^+$, [6,8,15,17-tetraphenylheptacene]$^+$).

Results and discussion

Our choice of HI as reductant was based on Harvey *et al.*'s earlier report[17] that polycyclic aromatic quinones are reduced to their corresponding arenes in good to excellent yield using HI or mixtures of HI and acetic acid. The addition of red phosphorus promoted further reduction to hydrogenated polycyclic aromatics. Harvey *et al.* did not extend their study to acenes, nor to acene quinones save 9,10-anthraquinone. We investigated acenes and acene quinones possessing between three and nine rings including several with phenyl substituents. We did not employ red phosphorus in any of our reactions. In nearly all cases studied, the acene and acene quinone reactants are reduced to hydrogenated acene species in excellent yield. Most interesting, acene and acene quinone molecules bearing pairs of phenyl substituents on alternating rings hydrogenate in a highly regioselective fashion. In these cases, the reductions generally occur at non-terminal rings and at rings without phenyl substituents. Table 1 lists the acene and acene quinone molecules tested, the hydrogenated acene products formed, and the percentage yield for each reaction.

Unsubstituted acenes and acene quinones with four or fewer rings are hydrogenated in regioselective fashion (entries 1, 2, 5, and 6 of Table 1). In each case, hydrogen adds across the

Table 1 Hydrogenation of acenes and acene quinones using HI–AcOH

Entry	Reactant	Product	% Yield (ratio)
1			99
2			99
3			99 (2 : 1)[a]
4			99
5			99
6			98
7			98 (1 : 2)
8			99 (0.2 : 1 : 7)
9			79 (2 : 1)
10			98
11			94
12			99
13		Complex mixture	49
14		Complex mixture	83
15	C_{60}	C_{3v} $C_{60}H_{18}$	90

[a] The *cis* and *trans* isomers of 9,10-dihydro-9,10-diphenylanthracene are not distinguished by NMR.

center-most ring which is arguably most aromatic and most reactive.[18] For pentacene, the difference in reactivity between the center-most ring and the other internal (penultimate) rings is diminished and this might be expected to translate into reduced regioselectivity. Indeed, the HI–AcOH reductions of pentacene, pentacene-6,13-dione and pentacene-5,7,12,14-tetraone (*i.e.*, entries 7–9 of Table 1) yielded multiple products in each case. However, there is still considerable selectivity in each of these reductions. Thus, only the three inside rings of the pentacene backbone are subject to hydrogenation, never the terminal rings. Moreover, adjacent interior rings are never simultaneously hydrogenated within a single product. The result is that either the center-most ring is hydrogenated alone or the two penultimate rings are hydrogenated.

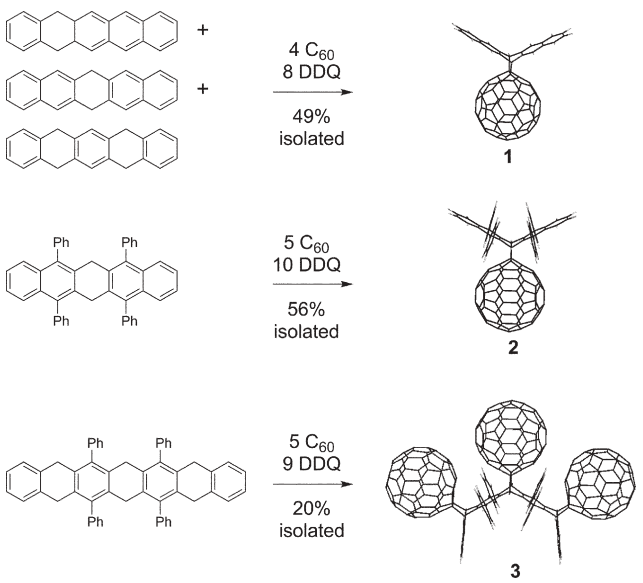
A major advantage of utilizing hydrogen as an acene protecting group is that one need not first prepare the parent acene. Instead, a corresponding acene quinone may be directly reduced. Acene quinones are much easier to synthesize than acenes and they have a long shelf-life. A general disadvantage of using acene quinones is that they exhibit poor solubility. However, poor solubility is not a limitation in the HI–AcOH reductions reported here. While several of the acene quinones form suspensions in HI–AcOH, they are slowly pulled into solution and they generally reduce in excellent yield. Interestingly, there is no preference for reduction at the carbon atoms that formerly bore carbonyl functions. For example, pentacene-6,13-dione yields seven times more 5,7,12,14-tetrahydropentacene than 6,13-dihydropentacene (entry 8 of Table 1) while pentacene-5,7,12,14-tetraone yields twice as much 6,13-dihydropentacene as 5,7,12,14-tetrahydropentacene (entry 9 of Table 1). These results indicate that the HI–AcOH reduction of a quinone species does not proceed directly to the hydrogenated acene products, but rather passes through an intermediate or a series of intermediates.

Highly regioselective hydrogenations are observed when pairs of phenyl substituents are positioned on alternating rings of the acene (*e.g.*, entries 3–4 and 10–12 of Table 1). In all cases but one (9,10-diphenylanthracene, entry 3), reduction occurs along the acene backbone at non-terminal rings that do not bear phenyl substituents. The corresponding hydrogenated acenes possess alternating aromatic and non-aromatic rings such that the terminal rings of the acene and the terphenyl moieties remain fully aromatic. Reduction at an unsubstituted, non-terminal backbone ring is not possible in 9,10-diphenylanthracene (entry 3 of Table 1). In this case, the observed formation of a mixture of *cis*- and *trans*-9,10-dihydro-9,10-diphenylanthracene reveals that reduction of the central ring of the terphenyl moiety is energetically preferred to reduction of a terminal ring along the acene backbone. On all larger phenyl substituted acenes, there appears to be an energetic driving force (*e.g.*, greater resonance delocalization energy) associated with reduction patterns in which terphenyl moieties remain intact.

The regioselective formation of 5,7,9,14,16,18-hexahydro-6,8,15,17-tetraphenylheptacene from 6,8,15,17-tetraphenyl-7,16-dione (entry 12 of Table 1) in near quantitative yield demonstrates that the HI–AcOH reduction can be extended to phenyl substituted acene quinones with more than five rings. Mondal *et al.* recently prepared an analogous dihydro species, 7,16-dihydro-6,8,15,17-tetraphenylheptacene, in 38% yield using a BH_3·THF reduction of the same quinone.[19] In addition to producing higher yields, the HI–AcOH conditions described here are apparently more vigorous as we observe no dihydro adduct.

The HI–AcOH reductions of unsubstituted heptacene-7,16-quinone and nonacene-7,9,18,20-tetraone (entries 13 and 14) lead in both cases to complex mixtures of products that could not be easily separated. Nonacenes and larger acenes are predicted to have singlet ground states with small singlet–triplet gaps and significant biradical character[20,21] making them highly interesting species for further study. They are however highly reactive and have yet to be isolated. H-Protection of suitably substituted nonacene quinones and larger acene quinones offers a potentially convenient means to prepare stable precursors. We are currently working to prepare H-protected, phenyl substituted nonacenes and undecacenes.

In order for H-protected acenes to be valuable intermediates for the construction of new molecules and materials, they must be readily deprotected. Likewise, we successfully formed 6,13-[60]fulleren-6,13-dihydropentacene, **1**, 6,13-[60]fulleren-6,13-dihydro-5,7,12,14-tetraphenylpentacene, **2**, and *cis*,*cis*-5,18-[60]fulleren-7,16-[60]fulleren-9,14-[60]fulleren-5,7,9,14,16,18-hexahydro-6,8,15,17-tetraphenylheptacene, **3**, *via* simple DDQ deprotections of the corresponding H-protected acenes in the presence of [60]fullerene. Thus, a mixture of hydrogenated pentacenes (entry 8, Table 1), 6,13-dihydro-5,7,12,14-tetraphenylpentacene (entry 11, Table 1), and 5,7,9,14,16,18-hexahydro-6,8,15,17-tetraphenylheptacene[22] (entry 12, Table 1) were separately deprotected using DDQ in the presence of [60]fullerene to generate **1**, **2**, and **3**, respectively (Scheme 1). The successful formation of **1** from a mixture of hydrogenated pentacenes demonstrates that the mixtures need not be separated before deprotection as they all converge on the same acene during deprotection. While the 49% yield of **1** is lower than the 59% yield obtained in the direct reaction between [60]fullerene and pentacene,[23] the 56%



Scheme 1 Formation of [60]fullerene-acene adducts using H-protected acenes as reactants.

isolated yield of **2** is a marked improvement over the 24% yield obtained in the direct reaction between [60]fullerene and 5,7,12,14-tetraphenylpentacene.[24] The low yield of **2** obtained in the direct reaction between [60]fullerene and 5,7,12,14-tetraphenylpentacene is attributable to the instability of the acene and the difficulties associated with its handling. Preparing and reacting 5,7,12,14-tetraphenylpentacene *in situ via* a DDQ deprotection of 6,13-dihydro-5,7,12,14-tetraphenylpentacene is a superior procedure. The use of H-protected acenes has even more advantages as the length of the acene increases. Indeed, the instability associated with heptacenes has complicated the isolation of 6,8,15,17-tetraphenylheptacene. Trisadduct **3** was nonetheless prepared without complication *via* the *in situ* deprotection of 5,7,9,14,16,18-hexahydro-6,8,15,17-tetraphenylheptacene.[22]

Given our success in preparing H-protected acenes using HI–AcOH and our general interest in fullerene chemistry, we attempted an HI–AcOH reduction of a very different polycyclic aromatic hydrocarbon, namely [60]fullerene. Because [60]fullerene is not soluble in acetic acid, it was dissolved in a 10 : 5 : 1 volume mixture of *o*-dichlorobenzene, acetic acid and 47% aqueous HI. The resulting two-phase mixture was heated to boiling under nitrogen in the dark for five days. Following standard work-up, a green powder was isolated in 90% yield. ^{1}H and ^{13}C NMR and LDI mass spectral characterizations revealed it to be C_{3v} $C_{60}H_{18}$, a known molecule[25] that was recently prepared in high yield using both a polyamine reduction[26] and a high temperature, high pressure direct hydrogenation.[27]

Conclusions and future direction

We have performed the first systematic study concerning the hydrogenation of acenes and acene quinones. In all cases, mixtures of HI and acetic acid were utilized as reductant. Hydrogenations of unsubstituted pentacenes and smaller acenes proceed in regioselective fashion. Phenyl substituted acenes and acene quinones have also been examined for systems up to and including seven contiguous rings (*i.e.*, heptacene backbone). In these cases, the reductions are highly regioselective and the corresponding H-protected acenes are stable species that show vastly improved solubility. H-Protected acenes may be deprotected using common dehydrogenation reagents such as DDQ. In this manner, three [60]fullerene-acene adducts have been prepared, including a *cis*,*cis*-tris[60]fullerene adduct of 6,8,15,17-tetraphenylheptacene, **3**, *via in situ* [60]fullerene trapping of the reactive acenes. Finally, a modified HI–AcOH reduction was successfully utilized to convert [60]fullerene into C_{3v} symmetric $C_{60}H_{18}$ in excellent yield. It is anticipated that H-protection will provide access to suitably substituted larger acenes like phenylated nonacenes and undecacenes. These systems should possess extraordinary physical and chemical properties and we are currently working to prepare them.

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