The Shapiro reaction of barrelene derivatives: the influence of annelation on acene formation

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The possible formation of pentacene from a tosylhydrazone of 6,13-dihydro-6,13-ethenopentacene under the conditions of the Shapiro reaction is explored, as previous work demonstrated that the tosylhydrazone of barrelene (bicyclo[2.2.2]octatriene) yields benzene under these conditions [C. Weitemeyer, T. Preuß, and A. de Meijere, *Chem. Ber.*, 1985, **118**, 3993]. The computational analyses based on homodesmotic equations involving the anions, and monomeric (including the dimethyl ether solvate) and dimeric organolithium compounds reveals that benzene formation is exothermic, but pentacene formation is endothermic due to the increased stability of the lithium derivative and the decreased stability of pentacene. The computational predictions are confirmed by experimental investigations.
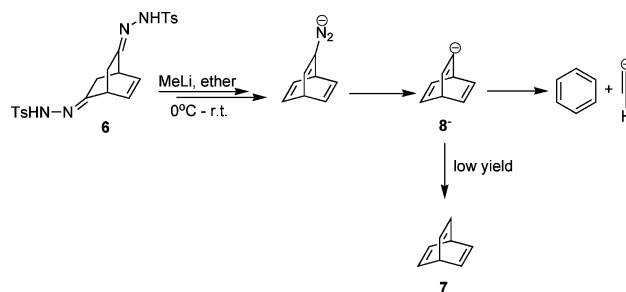
Introduction

The Shapiro reaction is a versatile method for transforming aldehydes and ketones **1** into alkenes **2** by reaction of the tosylhydrazone **3** with at least two equivalents of strong base (*n*-BuLi or MeLi) followed by aqueous work-up (see Scheme 1).[1–3] The generally accepted mechanism of the Shapiro reaction involves the deprotonation of the tosylhydrazone NH followed by that of an α-CH group. The resulting dianion **4** eliminates first *p*-toluenesulfinate and then N_2; protonation of the generated vinylanion **5** finally yields the desired alkene.
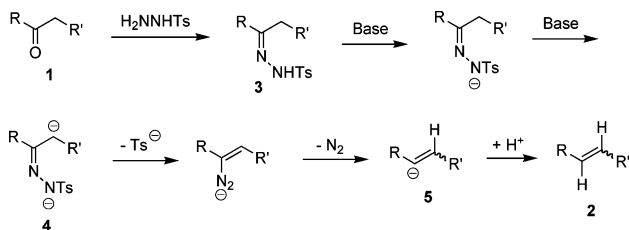
Scheme 1 Mechanism of the Shapiro reaction for the transformation of ketones into alkenes.

Shortcomings of the Shapiro reaction have been overcome by modifications with respect to the nature of the base and the hydrazone,[4–6] while problems with substrates which only have tertiary α-CH groups could also be solved.[7]

However, some substrates give the expected alkene products in only very low yield. A case in point is the reaction of the bis(tosylhydrazone) **6** with strong base described by de Meijere's group in 1985.[8] Benzene is obtained as the major product, and only small amounts of the desired Shapiro reaction product barrelene **7** were detected. Earlier, Jefford *et al.*[9] had reported low yields (12%) of **7** accompanied by benzene in the Shapiro reaction of **6**. Benzene formation was rationalized by a retro Diels–Alder reaction of the thermally labile 2-barrelenyl anion **8⁻** (see Scheme 2).

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Scheme 2 De Meijere's[8] 1985 observation of a retro Diels–Alder reaction rather than the anticipated Shapiro reaction.

The purpose of the present investigation is to delineate the influence of annelation on the stability of the corresponding anion under Shapiro conditions. The preferred reaction product, the conventional Shapiro alkene or the acene, is expected to depend critically on the stability of the aromatic hydrocarbon. While the acenes are less stable than benzene, it is not clear *a priori* if this will tip the balance in favor of the conventional Shapiro reaction or will allow a novel access to this class of aromatic hydrocarbons. Among them, pentacene is of particular interest as an active material in organic electronic applications, but it suffers from low solubility making the reliable production of devices challenging.[10–13] There is thus currently considerable interest in finding approaches for the generation of pentacene and higher acenes from soluble precursors under mild thermal[14–18] or photochemical[19–22] conditions. Therefore, the focus of the present investigation is on the possible formation of pentacene by fragmentation of the corresponding alkenyl anion **9⁻**.

Results and discussion

The question of the stability of **8⁻** and **9⁻**, or more specifically of their lithium derivatives **8**-Li and **9**-Li, should in principle be tractable by computational techniques. But this is challenging due to the tendency of organolithium compounds to form aggregates of varying size in solution and to strongly interact with ethereal

solvents. In addition, there is no information available on the aggregation of **8**-Li and **9**-Li in solution. We thus decided to focus on the inherent stability of the free anions **8**$^-$ and **9**$^-$ as well as their monomeric (**8**-Li and **9**-Li) and dimeric [(**8**-Li)$_2$ and (**9**-Li)$_2$] lithium derivatives towards acene formation. We do not consider any higher aggregates, but consider the interaction of monomers with two dimethyl ether molecules [**8**-Li·(OMe$_2$)$_2$ and **9**-Li·(OMe$_2$)$_2$]. The computations used density functional theory in conjunction with a polarized triple-ζ basis set (RI-BP86/TZVP). The conformations of dimers of lithium compounds are based on previous experimental and computational studies of vinyl- and ethynyllithium and were found to correspond to minima within the point group constraints given in Fig. 1.[23–26] In particular, we only considered the *anti* isomers as Fressigné *et al.*[23] have shown for vinyllithium that this conformer is slightly more stable than its *syn* form.
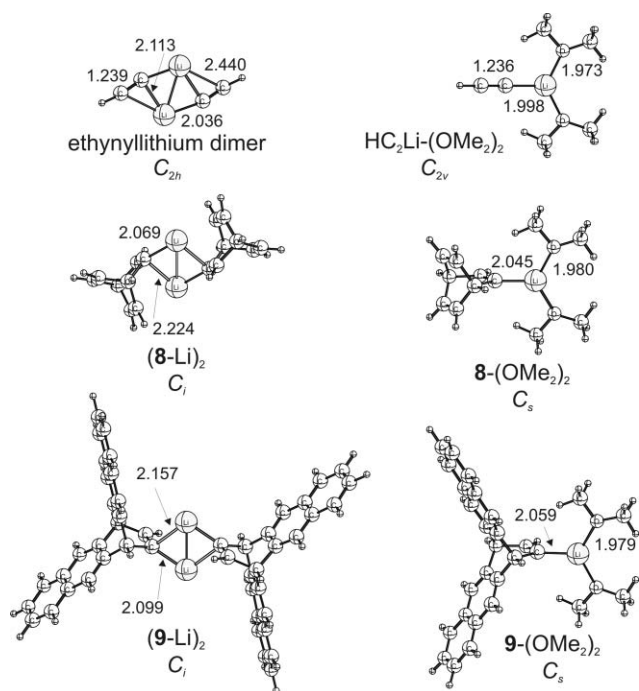

Fig. 1 Structures (RI-BP86/TZVP) of the dimethyl ether solvates and the dimers of the lithium compounds of interest in the present investigation. The Li–C and O–Li distances are given in Å.

The retro Diels–Alder reaction yielding benzene is exothermic in the gas phase for both the anion [eqn (1)], the corresponding monomeric (**8**-Li) and dimeric [(**8**-Li)$_2$] lithium compounds, as well as for the dimethyl ether solvate of **8**-Li. This finding is in agreement with the formation of benzene in the reaction of **6** with methyllithium as reported by de Meijere *et al.*[8] The three lithium containing models give similar reaction enthalpies, while reaction for the naked anion is less exothermic. This consistency of computational results is also observed for formation of the acenes ranging from naphthalene to pentacene (Table 1); thus, we focus on the data obtained for the dimers (RLi)$_2$ in the following discussion. The first and second annelation of the system ($n = 1$ and $m = 0$; $n = m = 1$) disfavor acene formation by an almost constant 13–14 kcal mol^{-1}, while the second set of annelated rings has a smaller disfavoring effect of about 5–6 kcal mol^{-1} per additional

Table 1 Reaction enthalpies [eqn (1)] at 298.15 K ($\Delta_R H(298.15\text{K})$ in kcal mol^{-1}) for formation of acenes from anions or organolithium compounds as computed at the RI-BP86/TZVP level of theory

Product	n	m	R$^-$	RLi	RLi·2OMe$_2$	$\frac{1}{2}$(RLi)$_2$
Benzene	0	0	−17.7	−23.0	−24.3	−23.7
Naphthalene	1	0	2.1	−8.3	−9.0	−10.7
Anthracene	1	1	22.5	8.4	8.0	3.6
Tetracene	2	1	31.1	14.3	14.1	9.7
Pentacene	2	2	39.7	20.6	20.5	14.8

ring ($n = 2$ and $m = 1$; $n = m = 2$). Thus only naphthalene formation is exothermic (for the organolithium compounds), while the formation of all higher acenes is endothermic.
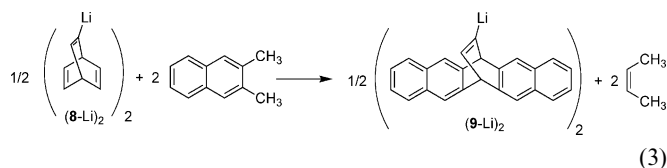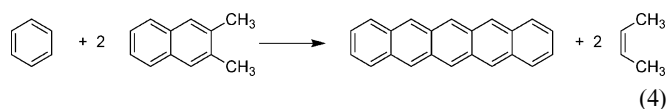

(1)
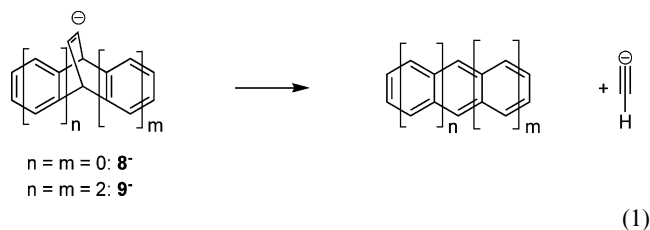
In an attempt to find more favorable conditions for pentacene formation, the reaction depicted in eqn (2) was also investigated.


(2)
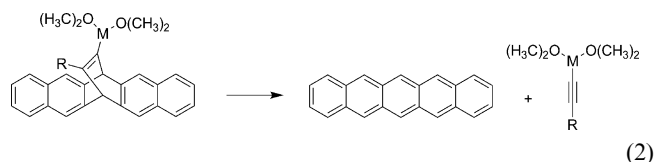
However, the reaction enthalpy hardly changes upon introduction of a phenyl group (R = Ph, M = Li: $\Delta_R H(298.15\text{K}) = 17.4$ kcal mol^{-1}) or a different metal ion (R = H, M = Na: $\Delta_R H(298.15\text{K}) = 21.4$ kcal mol^{-1}; R = H, M = K: $\Delta_R H(298.15\text{K}) = 21.5$ kcal mol^{-1}). The computational analysis thus shows that besides benzene only naphthalene formation is thermodynamically favorable. As there is no thermodynamic driving force for formation of the more interesting higher acenes, reaction barriers are not considered in this work.

The homodesmotic[27] eqn (3) and (4) allow the influence of the reactants and the products on the energy balances of eqn (1) to be dissected. We find that the reaction described by eqn (3) is exothermic by −9.7 kcal mol^{-1}; this shows that bisnaphthoannelation increases the stability of the organolithium compound **9**-Li. On the other hand, the reaction in eqn (4) is endothermic by 32.4 kcal mol^{-1}, and this indicates that twofold naphthoannelation destabilizes the aromatic system. Hence, this combination of stabilization and destabilization of the reactants and products, respectively, results in the pronounced dependence of the energy of the reaction in eqn (1) on n and m. This analysis is in agreement with the well-known higher reactivity of pentacene under Diels–Alder conditions with the central ring being the one of highest reactivity.[28–32]

(3)

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(4)

The computational analysis suggests that the Shapiro reaction of the tosylhydrazone **10** should not give the corresponding acene but rather the corresponding alkene **11**. As the computational data refers to the gas phase, we have attempted to experimentally verify the theoretical predictions for the pentacene system. Synthesis of the required tosylhydrazone **10** was achieved in three steps from the known[33] dinaphthobarrelene derivative **11** as outlined in Scheme 3.
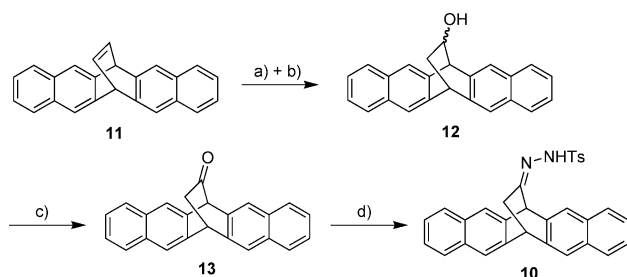

Scheme 3 Synthesis of the tosylhydrazone **10**. *Reagents and conditions*: a) BH₃·THF, THF, 0 °C; b) aq. NaOH, H₂O₂; yield: 73%; c) TEMPO, NaOCl, CH₂Cl₂, 0 °C to room temperature; yield: 71%; d) TsNHNH₂, MeOH–CH₃OH, reflux; yield: 69%.

It is noteworthy that initial attempts of *in situ* oxidation of the hydroboration product **12** with chromic acid following the protocol of Creary and Butchko were not met with success.[34] Instead of the expected ketone **13** the seven-membered ring ketone **14** was obtained along with some alcohol **12** (Scheme 4).
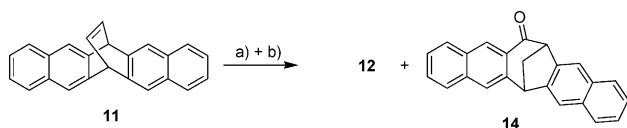
Scheme 4 *Reagents and conditions*: a) BH₃·THF, THF, 0 °C; b) chromic acid.

Formation of ketone **14** can be rationalized by a rearrangement which turns the secondary cation generated from **12** under acidic conditions into a stabilized benzyl cation (Scheme 5). Surprisingly, oxidation of the alcohol formed from this rearranged carbocation to the corresponding ketone **14** happens almost selectively. The oxidation of **12** to **13** under the acidic conditions was not observed.
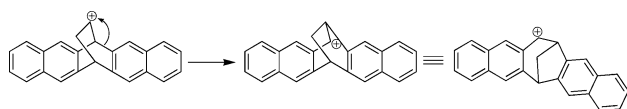
Scheme 5 Suggested mechanism for the formation of a benzylic cation.

Having the required tosylhydrazone available, its chemistry was investigated under Shapiro reaction conditions. The deprotonation of the α-CH group of **10** required rather drastic conditions: excess of *n*-BuLi in boiling diethyl ether. Under these conditions the Shapiro product **11** was obtained and there was no indication for the formation of pentacene (Scheme 6).

Hence, the experiment confirms the expectation based on the thermodynamic stability of the central intermediates **8⁻** and **9⁻**
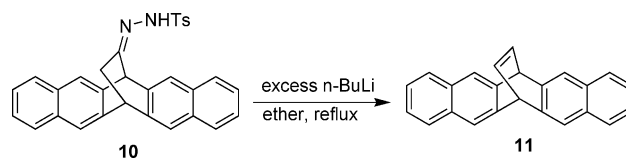
Scheme 6 Shapiro reaction of **10** yields **11** exclusively.

or their lithium derivatives obtained from approximate density functional computations. Even though an access to higher acenes *via* this route would have been highly desirable, the decreased stability of pentacene precludes its formation.

Conclusions

The theoretical analysis finds that successive annelation increasingly disfavors the retro Diels–Alder reaction of the barrelenyl anion **8⁻** observed by de Meijere[8] and favors instead the formation of the conventional Shapiro product. This is confirmed by an experimental investigation of the pentacene system for which a retro Diels–Alder reaction was not observed. The computational evaluation based on homodesmotic equations reveals that the differing reaction products under Shapiro conditions may largely be rationalized by the decreased stability of the hypothetical pentacene product compared to benzene. As the retro Diels–Alder reaction is unfavorable for **9**-Li, aqueous workup results in the dinaphthobarrelene product **11** rather than in pentacene. The formation of benzene under conditions of the Shapiro reaction observed earlier thus remains exceptional.[8]

Experimental and computational details

General

All reactions were carried out under a dry argon atmosphere in oven dried Schlenk type glassware with magnetic stirring. Temperatures are reported as bath temperatures. Et₂O was continuously refluxed and freshly distilled from sodium using benzophenone as indicator. All commercially available reagents were used without further purification, and were purchased from Aldrich Chemical Co., Acros Organics or Merck. *n*-BuLi was used as a 15% solution in hexane (1.59 M). TLC was performed on Al-backed plates coated with silica gel with F₂₅₄ indicator (Polygram SIL G/UV from Macherey-Nagel); the chromatograms were visualized under UV light (254 nm). ¹H and ¹³C NMR spectra were recorded in CDCl₃ with a Bruker DRX 400 and chemical shifts are reported in ppm downfield (δ) from TMS (tetramethylsilane). Mass spectrometry (EI, 70 eV) was performed with a VG Autospec. The intensities are reported as a percentage relative to the base peak after the corresponding *m/z* value. Matrix assisted laser desorption ionization (MALDI) spectra were obtained using a dithranol matrix with the instrument (N₂ laser, 337 nm) operating in reflector mode. FT-IR spectroscopy was performed with a Bruker Equinox 55 (KBr, ṽ in cm⁻¹).

6,13-Dihydro-14-hydroxy-6,13-ethanopentacene (12). A solution of 1 M BH₃·THF in THF (1 mL, 1 mmol) was added drop wise to a solution of 6,13-dihydro-6,13-ethenopentacene **11** (0.15 g, 0.5 mmol) in 30 mL of THF. The reaction mixture was stirred at 0 °C for 1 h and then allowed to reach rt slowly and continued to

stir for 4 h. The solution was cooled to 0 °C followed by addition of water (2 mL), 2 N aq. NaOH (1.5 mL) and 35% H$_2$O$_2$ (0.2 mL). The reaction mixture was allowed to stir overnight at rt. The aqueous phase was saturated with brine solution and the organic phase was extracted with dichloromethane. The organic extract was dried over sodium sulfate and concentrated on a rotary evaporator. The residue was subjected to column chromatography [silica gel, 80% (vol.) dichloromethane in hexane] to yield **12** (0.11 g, yield 73%). Mp 246–248 °C; IR 3553 (O–H), 3053, 2951, 1498, 755; ^{1}H-NMR (400 MHz) 1.60 (dt, 1 H, J = 13.6, 2.8 Hz), 2.51 (m, 1 H), 4.36 (dt, 1 H, J = 9.1, 3 Hz), 4.50 (t, 1 H, J = 2.8 Hz), 4.61 (d, 1 H, J = 3.3 Hz), 7.41 (m, 4 H), 7.70 (s, 1H), 7.77 (m, 6 H), 7.85 (s, 1 H); ^{13}C-NMR (100 MHz) 39.83, 43.83, 52.39, 69.86, 121.58, 121.72, 123.31, 125.30, 125.52, 125.54, 125.70, 125.74, 127.51, 127.56, 132.36, 132.43, 132.69, 132.88, 136.06, 138.1, 140.69, 141.04; mass spectrum (EI), m/e M$^+$ 322(7), 304(14), 289(4), 278(100), 151(4), 139(37), 126(5); HRMS (EI) m/z = 322.137146 (M$^+$), calcd m/z = 322.135765.

6,13-Dihydro-14-oxo-6,13-ethanopentacene (13). Compound **12** (0.13 g, 0.4 mmol) was dissolved in 20 mL of dichloromethane and cooled to 0 °C. TEMPO (0.02 g), KBr (0.10 g), and 1 mL of water was added to the solution, followed by the addition of 6 mL of sat. NaHCO$_3$ and 6 mL of sat. NaOCl. The reaction mixture was stirred at 0 °C for 3 h and then allowed to reach rt slowly and continued to stir for an additional 1 h. The solution was cooled to 0 °C followed by addition of water (2 mL), 2 N aq. NaOH (1.5 mL) and 35% H$_2$O$_2$ (0.2 mL). The aqueous phase was saturated with brine solution and the organic phase was extracted with dichloromethane. The organic extract was dried over sodium sulfate and concentrated on a rotary evaporator. The residue was subjected to column chromatography [silica gel, 50% (vol.) dichloromethane in hexane] to yield **13** (0.092 g, yield 71%). Mp >296 °C; IR 3054.5, 2951, 1722, 866, 758; ^{1}H-NMR (400 MHz) 2.57 (d, 2 H, J = 2.8 Hz), 4.80 (t, 1 H, J = 2.5 Hz), 5.08 (s, 1 H), 7.44 (m, 4 H), 7.78 (m, 4H), 7.83 (s, 2 H), 7.84 (s, 2 H); ^{13}C-NMR (100 MHz) 40.55, 44.67, 62.84, 122.40, 124.33, 126.04, 126.28, 127.62, 127.74, 132.50, 132.96, 134.36, 139.51, 205.34; mass spectrum (EI), m/e M$^+$ 320(2), 291(7), 289(7), 278(100), 139(25); HRMS (EI) m/z = 320.121643 (M$^+$), calcd m/z = 320.120115.

6,13-Dihydro-14-tosylhydrazono-6,13-ethanopentacene (10). A suspension was made by adding tosyl hydrazine (0.043 g, 0.23 mmol) and ketone **13** (0.074 g, 0.23 mmol) in 40 mL of 1 : 1 CH$_3$OH–CH$_3$CN. The mixture was then allowed to stir vigorously under reflux for 1 day. Additional tosyl hydrazine (0.021 g, 0.11 mmol) was added to the solution and refluxed for an additional day. The reaction mixture was concentrated on a rotary evaporator and subjected to column chromatography (silica gel, dichloromethane) to yield **10** (0.045 g, yield 69%). Mp 149 °C (decomp.); IR 3434 (N–H), 1633; ^{1}H-NMR (200 MHz) 2.28 (s, 3 H), 2.48 (d, 2 H, J = 2.78 Hz), 4.75 (t, 1 H, J = 2.5 Hz); 5.21 (s, 1 H), 7.08 (broad, 1 H), 7.19 (d, 2 H, J = 8 Hz), 7.42 (dd, 4 H, J = 3.3, 3.3 Hz), 7.75 (m, 10 H). ^{13}C-NMR (50 MHz) 20.43, 28.68, 32.12, 42.81, 121.13, 121.39, 122.34, 124.97, 125.03, 125.08, 125.26, 126.56, 126.69, 126.85, 128.52, 131.48, 131.53, 134.29, 135.56, 138.54, 143.04, 157.92; mass spectrum (MALDI), m/e M + H$^+$ 489.25.

6,14-Dihydro-6,14-methanocyclohepta[1,2-b;4,5-b′]dinaphthalen-13-one (14). A solution of 1 M BH$_3$·THF in THF (1.4 mL, 1.4 mmol) was added drop wise to a solution of **1** (0.20 g, 7 mmol) in 30 mL of THF. The reaction mixture was stirred at 0 °C for 1 h and then allowed to reach rt slowly and continued to stir for 4 h. The solution was cooled to 0 °C followed by addition of water (1.4 mL) and chromic acid (1.4 mL). The reaction mixture was allowed to reach rt and continued to stir for 4 h. The aqueous phase was saturated with brine solution and the organic phase was extracted with dichloromethane. The organic extract was dried over sodium sulfate and concentrated on a rotary evaporator. The residue was subjected to column chromatography [silica gel, 50–80% (vol.) dichloromethane in hexane] to yield **12** (0.10 g, yield 47%) and **14** (0.08 g, 38%). Mp >296 °C; IR 3053.5, 2948.5, 1723.5, 1688, 1624, 1598, 1194, 748; ^{1}H-NMR (400 MHz) 2.91 (d, 1 H, J = 11 Hz), 2.98 (m, 1 H), 4.28 (d, 1 H, J = 4.4 Hz), 4.55 (d, 1 H, J = 4.5 Hz), 7.37 (m, 2 H), 7.41 (m, 1H), 7.53 (m, 1 H), 7.68 (m, 1 H), 7.73 (m, 2 H), 7.76 (s, 1 H), 7.81 (m, 2 H), 7.88 (s, 1H), 8.47 (s, 1 H); ^{13}C-NMR (100 MHz) 45.66, 47.90, 56.80, 121.60, 122.70, 124.20, 125.80, 126.03, 126.09, 126.27, 127.31, 127.57, 127.67, 128.01, 128.76, 129.92, 130.53, 132.22, 133.08, 133.39, 135.93, 137.87, 142.90, 146.74, 195.50; mass spectrum (EI), m/e M$^+$ 320(100), 303(21), 291(28), 289(30), 278(58), 265(7), 160(9), 144(18), 139(15); HRMS (EI) m/z = 320.118164 (M$^+$), calcd m/z = 320.120115.

General procedure for Shapiro reaction of 10. 0.1 mL (0.24 mmol) of *n*-butyllithium in hexanes ($\sim$2.4 M) was added to a solution of **10** (30 mg, 0.06 mmol) in 15 mL of dry ether at −78 °C under argon. The reaction mixture was allowed to reach rt and was refluxed overnight. ^{1}H-NMR of the crude reaction mixture indicated the formation of **11**. Similar procedures were followed using methyllithium and *tert*-butyllithium as bases. The reactions were monitored by UV-vis spectroscopy of the reaction mixtures at different stages. Formation of pentacene was not observed in any case.

Computations

Density functional computations employed the BP86[35,36] functional in conjunction with the TZVP basis set of the Ahlrichs group.[37] The resolution-of-the-identiy (RI) procedure was employed along with the fitting basis sets implemented in the Turbomole program.[38,39] Geometries were completely optimized and harmonic vibrational frequencies[40] were computed to verify that the obtained structures correspond to minima and to obtain the zero-point vibrational energies. Improved numerical accuracy was obtained by changing the grid size for integration and the SCF convergence threshold to m4 and to 10^{-8}, respectively.

Acknowledgements

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