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Acene Homologues

Photogeneration of Octacene and Nonacene**

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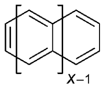
Dedicated to Professor Paul von Ragué Schleyer on the occasion of his 80th birthday

The chances of studying parent acenes **1** larger than heptacene (**2**) are generally considered slim. Clar, a pioneer in the field of acene chemistry, concluded in the 1964 edition of his textbook that "the syntheses of octacene could succeed seems remote."[1] Even the possibility of synthesizing heptacene was debated following Clar's pioneering efforts in 1942.[2–5] It was achieved only in 2006 by the ingenious utilization of a polymethylmethacrylate (PMMA) matrix at room temperature.[6] Subsequent investigations in solid noble gases at 10 K allowed the analysis of the electronic structure, stability, and photoionization of heptacene.[7,8]



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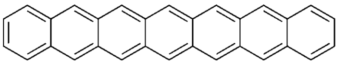

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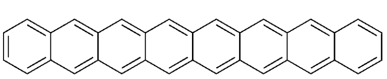

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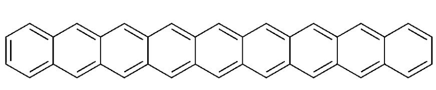

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The shorter acenes enjoy considerable attention because their planar geometry and electronic structures make them good candidates for applications as organic electronic materials.[5,9–11] For example, pentacene (**1**, $x=5$) is the best available organic p-type semiconductor, but the larger members could be even more useful.[10] Their investigation, however, is hampered by the quickly increasing reactivity within the acenes series[12] that currently limits experimental research in this area to heptacene. Recent work has shown that bulky substituents kinetically stabilize the heptacene framework, thus providing interesting compounds for materials applications.[13–15]

Clar's discouraging statement surely refers to experiments under conventional conditions at room temperature. By using cryogenic matrix-isolation techniques, we have defied Clar's prediction and herein report the synthesis of octacene (**3**) and nonacene (**4**). Our approach relies upon a protecting-group strategy based on the photochemically induced bisdecarbonylation of bridged α-diketones, sometimes called the Strating–Zwanenburg reaction.[16] This reaction has been used for acene synthesis previously,[16,17] most notably by Neckers and co-workers for the synthesis of hexacene (**1**, $x=6$) and heptacene (**2**) in PMMA.[6,18] In our experiments, the photobisdecarbonylation is performed at 30 K in an argon matrix that stabilizes the reactive acene.

Acene photoprecursors **5** and **6** were designed such that they do not contain segments larger than anthracene to ensure stability and solubility. The known 5,6,7,8-tetramethylenebicyclo[2.2.2]oct-2-ene[19] (**7**) is used as a building block for constructing the oligoacene framework of **8** and **9** by successive Diels–Alder reactions followed by aromatization (Scheme 1). Without separation, the two possible stereoisomers of **8** and **9** were transformed into the tetraketones **5** and **6** by dihydroxylation and oxidation. The last step proved to be particularly difficult, as we were not able to produce **5** or **6** by Swern oxidation. Likewise, attempts using *o*-iodoxybenzoic acid in DMSO proved to be unsuccessful.[20] Ultimately, the reaction with TEMPO/NaOCl gave **5** and **6**.[21]

The UV/Vis spectra of the higher oligoacenes are characterized by weak long-wavelength and intense short-wavelength absorptions, known as p and β bands, respectively.[1,8,22] It is well known that these characteristic transitions shift to longer wavelengths with increasing system size. Hence, these spectroscopic signatures of oligoacenes provide a reliable means of identification for octacene and nonacene.

Compounds **5** and **6** can be sublimed under the high-vacuum conditions required for matrix isolation. Compound **6** shows the typical UV/Vis transitions in the 500–350 nm range arising from the $n \rightarrow \pi^*$ transitions of the bridging α-diketone units, while the stronger β bands of the acene subunits are observed at 259 and 277 nm (Figure 1 a). Upon irradiation with visible light ($\lambda > 360$ nm), the bands of **6** decrease and new ones increase with isosbestic points. The new intense

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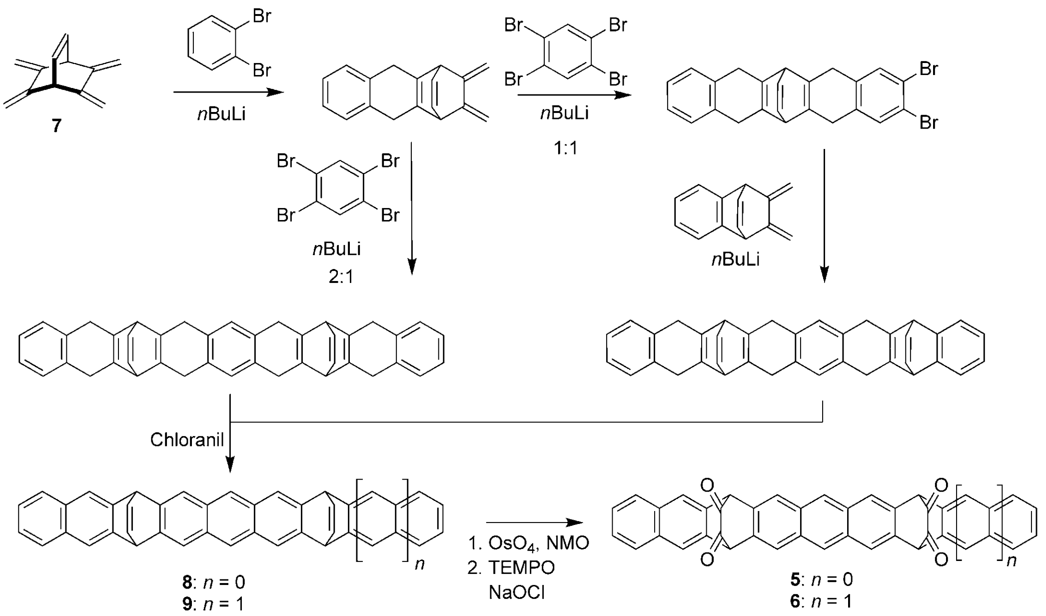
Supporting information for this article (experimental details, spectral data, and characterization of novel compounds as well as large-scale UV/Vis/NIR spectra of octacene and nonacene generation in matrices) is available on the WWW under http://dx.doi.org/10.1002/anie.200906355.



Scheme 1. Synthesis of photoprecursors **5** and **6** for octacene (**3**) and nonacene (**4**). For details see the Supporting Information. NMO = *N*-methylmorpholine-*N*-oxide, TEMPO = 2,2,6,6-tetramethylpiperidine-1-oxyl.

β band at 321 nm and weak p band with $\lambda_{max} = 666$ nm are clearly too high in energy to be associated with nonacene.

Because hexacene itself has β and p bands at 311 and 655 nm, respectively, in solid argon,[8] we assign the photoproduct as **10**, which contains a hexacene subunit formed upon photocleavage of one of the two α-diketone bridges (Scheme 2). The characteristic hexacene absorbance at 321 nm can be recognized after sublimation and before irradiation as a weak feature in the spectrum, indicating that **6** sublimes with partial decomposition to **10**.

However, additional weak signals at 339 and 865 nm can be detected after prolonged visible-light irradiation ($\lambda > 360$ nm), and these increase further upon UV irradiation ($\lambda = 305$–320 nm, see Figure 1 b). At the same time, signals due to **10** decrease in intensity and isosbestic points are observed. After prolonged UV irradiation, the signals due to **10** have essentially disappeared and a new species dominates the spectrum with strong absorptions at 339 and 418 nm, and weaker typical p-band signals extending up to 865 nm. Based on this pronounced bathochromic shift of the typical acene transitions, this newly formed species is assigned to nonacene (**4**), which arises from **10** upon irradiation at shorter wavelengths (Scheme 2).

The shorter tetraketone **5** shows similar stepwise photochemistry: long-wavelength irradiation mainly cleaves one of the diketone bridges, while formation of octacene (**3**) requires subsequent short-wavelength irradiation (see Figures S23–S25 in the Supporting Information for spectra). The typical electronic transitions are between the values measured previously for heptacene and here for nonacene (see Tables S1 and S2 in the Supporting Information for bands of **3** and **4**).

The assignment of **3** and **4** is supported by their photoionization. Irradiation at 185 nm generates NIR bands owing to acene radical anions and cations as observed in our earlier acene studies.[7,8] These intense NIR absorptions with $\lambda = 1772$ nm arise from the SOMO−1→SOMO transitions of the radical ions of nonacene (Figure 2). The corresponding transition for octacene radical ions is at 1476 nm (see Figure S26 in the Supporting Information), again between the values for heptacene and nonacene. Comparison of these transitions for all acenes studied by us ($x = 5$–9) shows that they shift linearly with acene size (Figure 3 a).

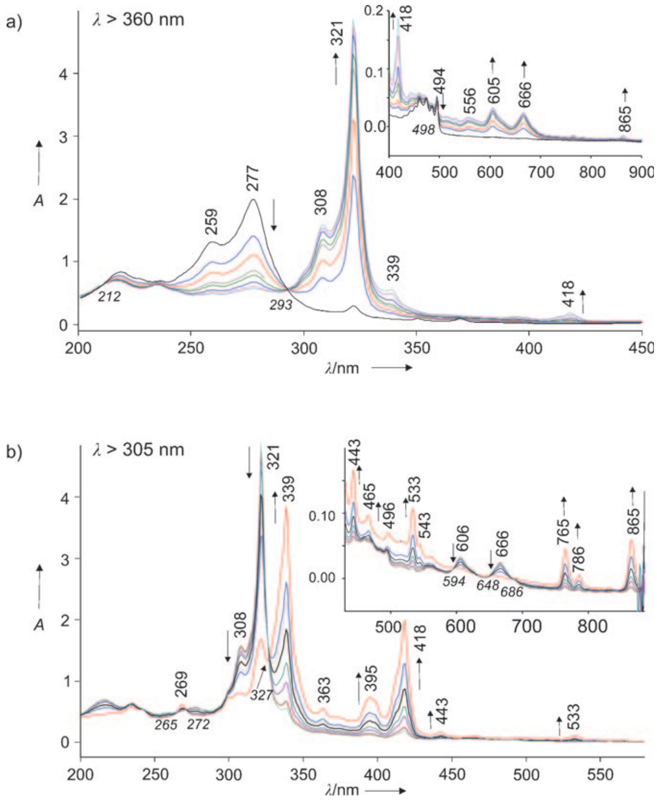
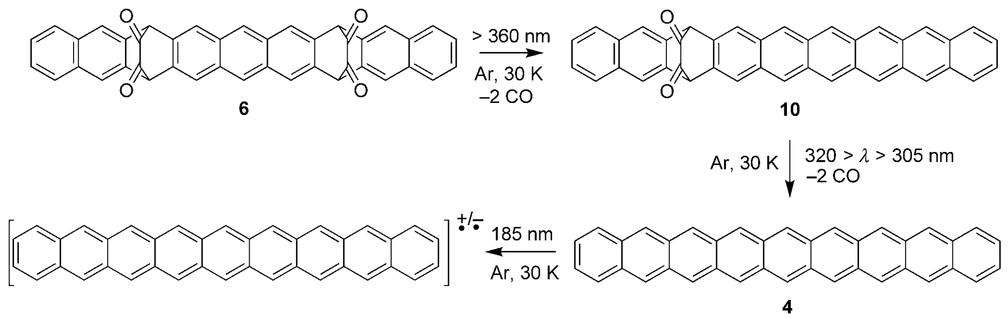


Figure 1. UV/Vis spectra showing the transformation of **6** into **4**. The direction of arrows indicates increasing or decreasing bands under the respective irradiation conditions. The values for isosbestic points are given in italics. a) Irradiation of **6** using visible light ($\lambda > 360$ nm). b) Subsequent UV irradiation ($\lambda = 305$–320 nm) results in the photogeneration of **4**. The spectrum in red was measured after irradiation overnight and was not used for determining isosbestic points because the optical quality of the argon matrix deteriorates under these conditions resulting in baseline shifts.



Scheme 2. Photochemical synthesis of nonacene (**4**) from **6** in solid argon at 30 K under matrix-isolation conditions.

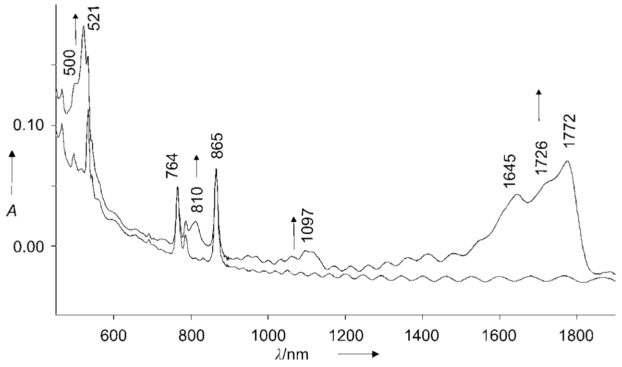


Figure 2. Vis/NIR spectrum obtained after irradiation ($\lambda = 185$ nm) of the nonacene sample prepared as described in the caption of Figure 1.

How far is the longest known acene from the polymer limit with respect to the photophysical properties? The longest-wavelength transitions, the p bands, in the longer acenes correspond to the $S_0 \rightarrow S_1$ excitations that mainly involve HOMO→LUMO transitions. A property also related to the HOMO–LUMO gap is the singlet–triplet energy splitting values computed for this energy difference can be fitted well with an exponential of the form $a + be^{-c}$.[23] The measured longest-wavelength transitions for the p bands of acenes under identical conditions ($x = 5$–9) can also be fitted with such an exponential function (Figure 3 b).[24] Assuming that no other optical transition falls below the p band, the optical gap of polyacene deduced from the exponential fit is (1054 ± 52) nm or (1.18 ± 0.06) eV. This corresponds to an effective conjugation length of about $x_{\mathrm{ECL}} \approx 24$–$25$.

Computational analyses suggest that heptacene and larger acenes should posses an antiferromagnetic (AFM) singlet ground state.[23,25] This analysis is in contrast to the extrapolation of experimental triplet energies from oligoacenes up to hexacene, which suggests that nonacene has a triplet ground state.[22] The regularity of spectroscopic data that we observe for nonacene and its radical ions is in support of the theoretical data. The additional strong absorption at 418 nm (377 nm for octacene) is of too short wavelength to be due to the triplet state[26] and may indeed be associated with the electronic structure of the AFM ground state. There is theoretical support for the emergence of an additional strong feature to the red of the β band for heptacene.[27] Further experimental and theoretical investigations of the higher acenes are highly desirable.

The results reported herein show that under suitable conditions the long-sought higher acenes octacene (**3**) and nonacene (**4**) are accessible and can be studied experimentally. This suggests that these extended π systems are reasonable targets for conventional synthesis if judiciously chosen substituents are included for kinetic stabilization. This will allow access to interesting novel organic material[28] for semiconductor applications.

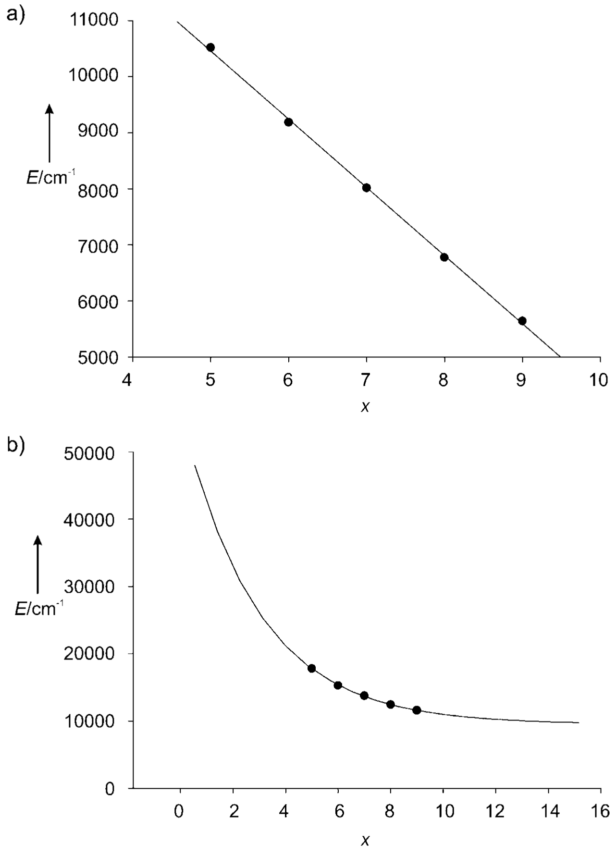


Figure 3. a) Linear behavior of the energies of the SOMO−1→SOMO transitions in acene radical cations $\mathbf{1}^{\bullet +}$ ($x = 5$–9) in solid argon; $R^2 = 0.9993$. b) Fitting the function $y = y_0 + ae^{-bx}$ to the p transition energies in acenes (dots) in solid argon results in $y_0 = (9490 \pm 450)$ cm^{-1}. Data for the oligomers with $x = 5$–7 were taken from reference [8].

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