Acene Dications

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Heptacene: Increased Persistence of a $4n+2$ π-Electron Polycyclic Aromatic Hydrocarbon by Oxidation to the $4n$ π-Electron Dication**

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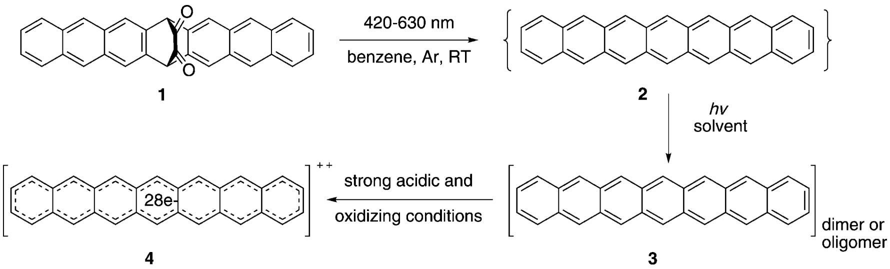
Although interest in heptacene goes back to the 1940s,[1,2] its isolation in substance or observation in solution could not be achieved beyond doubt.[2–5] The reactivity of acenes quickly increases with the number of annulated rings, as quantified by Biermann and Schmidt[6] who measured the rate constants for the Diels–Alder reaction with maleic anhydride. The longest acene they studied, hexacene, shows a second-order rate constant k_2 that is about 3000 times higher than that of anthracene, 70 times higher than that of tetracene, and at least 4 times higher than the rate constant of pentacene. For heptacene a further increase in its reactivity can be expected owing to its even larger π-system.

Neckers et al. generated heptacene (**2**) photochemically in a polymethylmethacrylate (PMMA) matrix by using the Strating–Zwanenburg reaction of bridged α-diketone **1**. Heptacene (**2**) in PMMA matrix disappears within about four hours at room temperature. This is due to reaction with atmospheric oxygen that diffuses into the PMMA film.[7] Heptacene cannot be isolated when α-diketone **1** is photolyzed in solution, only its triplet–triplet absorption could be observed by time resolved femtosecond spectroscopy.[9] Under cryogenic inert-gas matrix-isolation conditions the Strating–Zwanenburg reaction allows the study of the parent acenes from pentacene up to nonacene, along with their radical ions.[8–11] After evaporation of the noble gas matrix and warming the sample to room temperature, heptacene behaves exceptionally. Whereas the pentacene and hexacene can be recovered as monomers, heptacene forms dimers (**3**) or possibly even oligomers.[8] Recent theoretical work suggests that dimers of acenes larger than hexacene are thermodynamically more stable than the monomers, that dimerization involves only low barriers, and that polymers may be thermodynamically more stable than dimers.[12]

As part of our investigations in the field of acene chemistry, we report the unexpected formation of a persistent dicationic species of heptacene (**4**). This is one of the very rare examples of an alternating polycyclic hydrocarbon that has a dramatically increased persistence as a dication compared to its neutral compound (Scheme 1).



Scheme 1. Photo-bis-decarbonylation of α-diketone **1** leads to heptacene dimer/oligomer (**3**) from which its dication **4** is obtained under strong acidic and oxidizing conditions.

Irradiation of a saturated solution of α-diketone **1** in degassed benzene or in *o*-dichlorobenzene at room temperature under argon atmosphere leads to a precipitate **3** with an orange color similar to that of tetracene. Its poor solubility in common organic solvents hampers its characterization. Heating **3** in the chamber of an EI mass spectrometer to 250–300 °C produces heptacene $[M]^{+}$ at m/z 378 and $[M]^{++}$ at m/z 189. In addition, the mass of dihydroheptacenes was detected. The $[M+2]^{+}$ peak may result from dihydroheptacenes that are formed during photoreaction or by reduction with residual water in the ionization chamber.[13] The LDI-TOF mass spectra suggest formation of a heptacene dimer. But as certain hexacene dimers fragment into monomers during EI and LDI mass spectrometry,[14] the presence of higher oligomers cannot be excluded. The EI and LDI-TOF mass spectra show in addition masses of oxygenated heptacenes and heptacene dimers (see Supporting Information for discussion). The CP-MAS ^{13}C NMR spectrum (Figure S2) of the photoproduct **3** shows a large signal between $\delta = 121$ to 137 ppm with a maximum at $\delta = 127.8$ ppm and a shoulder at $\delta = 131.8$ ppm, and a smaller one at $\delta = 141.8$ ppm, all belonging to aromatic carbon atoms. A smaller signal at $\delta = 56.6$ ppm indicates bridgehead carbon atoms in heptacene dimers and/or oligomers (see Figure S1 for possible heptacene dimer structures).[14] The signals at $\delta = 32$ ppm is typical for dihydroacenes[15] which can also be found in our EI mass spectra.

The detection of heptacene in the EI-MS experiment indicates that dimerization may be reversible at temperatures above 250 °C. Unfortunately, all attempts to obtain heptacene

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by heating the photoproduct **3** under high vacuum only produced a brownish black film consisting, according to EI-MS, of dihydroheptacenes and oxygenation products.

Surprisingly the orange substance **3** dissolves far better in concentrated sulfuric acid than in organic solvents inducing a color change to slightly brownish green. Acenes dissolve in sulfuric acid under formation of intense colored solutions, a process that has indeed been used as a qualitative test in the early days of acene chemistry.[16] In sulfuric acid acenes are oxidized to radical cations (anthracene, tetracene, pentacene)[17] or even twice to dications (tetracene, pentacene, hexacene)[18] depending on the acid concentration. The optical spectrum of the brownish green solution of our photoproduct **3** in H_2SO_4 showed very intense absorption maxima at 435 nm and in the near infrared region at 944 nm indicating a small HOMO–LUMO gap of an extended π-system (see Figure 1). Other absorption maxima are located at 367, 577, and 832 nm. This data cannot easily be reconciled with a dimer or oligomer of heptacene. The heptacene radical cation shows a strong absorption at 1250 nm in solid argon.[8a] As the solvent effect is rather small for acene radical cations (see Figure 2), the spectrum of **3** in fuming sulfuric acid is not in agreement with that of the heptacene radical cation.

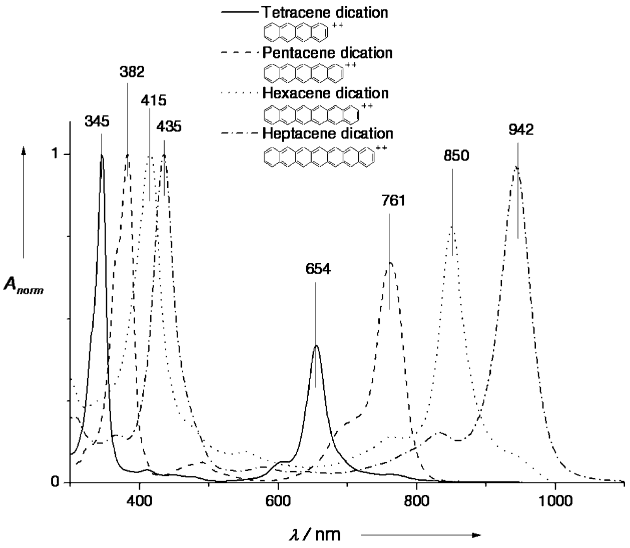


Figure 1. UV/Vis-NIR-spectra of acene dications from tetracene to heptacene in fuming sulfuric acid at room temperature.

We thus revisited the formation of the dications of anthracene, tetracene, pentacene, and hexacene and their behavior in sulfuric acid of varying concentrations.[17,18,20] The data we obtained for the dications by dissolving anthracene, tetracene, and pentacene in sulfuric acid are in good agreement with previous experiments,[16–18] but not with those reported by Manchado et al.[20] Lacking a sample of hexacene, we photolyzed 6,15-dihydro-6,15-ethanohexacene-17,18-dione (**5**) which produces hexacene only in the initial stages of photolysis, but results in an as yet uncharacterized material according Mondal et al.[10] By dissolving this material in sulfuric acid the data of the hexacene dication reported by Wirz et al.[18a] could be reproduced. Extrapolation of the data of the smaller dications gives a longest wavelength absorption of around 1.32 eV (940 nm) for the heptacene dication (see Figure 2). This value is in very good agreement with our observation (944 nm). The assignment is further supported by ab initio computations using spectroscopy oriented configuration interaction (SORCI) that arrive at transition wavelengths of 955 nm (to 1^1B_{3u}, oscillator strength $f = 1.07$) and 382 nm (to 2^1B_{3u}, $f = 3.67$).[21]

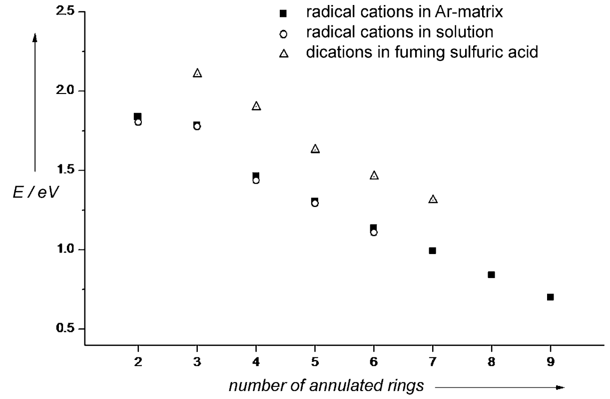


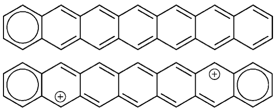
Figure 2. The SOMO−1→SOMO transition energies of acene radical cations in solution[17,18b] and cryogenic noble gas matrices[8,11,19] and HOMO–LUMO transition energies of acene dications in fuming sulfuric acid measured by ourselves.

The ^1H NMR spectrum of heptacene dication (**4**) in D_2SO_4 shows peaks at $\delta = 8.04, 8.29, 9.05, 9.40$, and 9.46 ppm. The spectrum is clearly different from that of heptacene-7,16-quinone (see Figure S7). The signals can be assigned based on COSY and NOESY experiments (see Supporting Information for details). The $^{13}C\{^1H\}$-NMR spectrum shows eight signals as required for the heptacene dication. The chemical shifts follow the trend of anthracene, tetracene, and pentacene dications.[22]

The heptacene dication (**4**) in sulfuric acid is stable for more than one year in the absence of water and oxygen, as evidenced by an unchanged UV/Vis-NIR spectrum. Unfortunately, attempts to isolate or crystallize the heptacene dication from the sulfuric acid solutions have not been successful to date.

The electronic structure of the heptacene dication was further investigated with help of a multireference self-consistent field method of the restricted active space type (RASSCF).[23] The adiabatic singlet–triplet (S_0–T_1) energy difference of heptacene (**2**) is 14.5 kcal mol^{-1} at the RASSCF level, in good agreement with the benchmark coupled cluster theory based focal point analysis value of 18 kcal mol^{-1}.[24] The singlet–triplet energy gap is larger for the dication, 19.2 kcal mol^{-1} at the RASSCF level. An inspection of the RASSCF wave function for the singlet ground state shows that the weight of the Hartree–Fock configuration is smaller in the neutral species (neutral: 0.56; dication: 0.87), while that of the second most important configuration (doubly excited $H^2 \rightarrow L^2$) is larger (neutral: 0.13; dication: 0.06). By this measure, the diradical character of the dication is smaller than that of neutral heptacene.[25] The diradical character of heptacene might be the explanation for the high reactivity towards oxygen in our experiments.

Heptacene has 30 π electrons and this is at least formally a $4n+2$ Hückel aromatic compound, even though there is only one aromatic sextet that needs to be shared among the seven rings (Scheme 2).[26] Two-electron oxidation to the dication results in $4n$ π electron system, but this can in principle be written with two aromatic sextets.[26] A computational analysis for anthracene concluded that the doubly charged system indeed can be drawn with two Clar sextets.[27]



Scheme 2. Neutral heptacene and heptacene dication with their Clar sextets

The results herein show that for acenes the tendency to dimerize (or oligomerize) increases with growing size of the π system while in return their dications are formed more and more easily in sulfuric acid. It was unexpected that the hexacene and heptacene dications can be obtained from the dimers or oligomers that form during photogeneration in solution rather than from the monomers themselves. It is very remarkable that the heptacene dication is persistent for more than one year now in sulfuric acid solution, while neutral heptacene is a highly reactive species. The primary mode of decomposition of higher acenes in the absence of oxygen is dimerization, a pathway that is blocked as a result of the Coulomb repulsion of the dications.

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