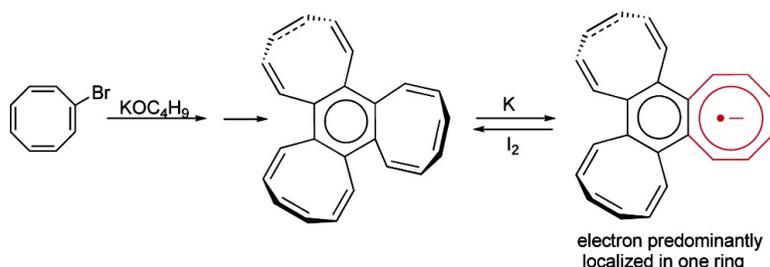


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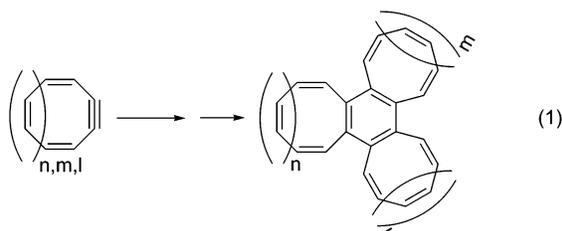
The Second Triannulenylyene: Tri-[8]annulenylyene

Matthew K. Kieseewetter, Richard C. Reiter, and Cheryl D. Stevenson*

Department of Chemistry, Illinois State University, Normal, Illinois 61790-4160

Received February 20, 2004; E-mail: cdsteve@ilstu.edu

The interesting properties of triphenylene [(C₆H₄)₃] have fascinated chemists¹ since its discovery in 1867.² Its fluorescence, UV absorption, and recent use in triphenylene-based discotic (columnar) liquid crystalline materials, which have potential electronic applications,³ further augment the intense interest in this compound. Indeed, an entire review article has been devoted to this one molecule.¹ Despite the plethora of recent articles about this 18-carbon system,⁴ we need to remain cognizant of the fact that it represents the only known member of the triannulenylyenes, a class of compounds defined by the bringing together of three annulynes, as in reaction 1.



Benzyne dimerizes to form biphenylene, but the reaction sequence leading to (C₆H₄)₃ does not involve three molecules of benzyne as originally thought.¹ Using reaction conditions that are analogous to those involving [6]annulyne (benzyne) and leading to triphenylene (*n*, *m*, *l* = 0), we have formed the second triannulenylyene (tri-[8]annulenylyene) from [8]annulyne (*n*, *m*, *l* = 1).

Monobromocyclooctatetraene (C₈H₇Br) is known to undergo dehydrohalogenation to form [8]annulyne (C₈H₆), which can be trapped as a stable (under low-temperature conditions) anion radical.⁵ Under high-vacuum conditions, when C₈H₇Br is treated with potassium-*tert*-butoxide in hexamethylphosphoramide (HMPA),⁶ a deep green solution is formed. Immediate exposure of this room-temperature solution to a potassium metal mirror results in a brownish solution, which yields the EPR spectrum of the bi-[8]-annulenylyene [(C₈H₆)₂] anion radical.⁷

However, if the green solution is allowed to sit for a few seconds prior to exposure to the metal mirror, the EPR spectrum shown in Figure 1 can be recorded. Even if exposure of the solution to the metal surface occurs too early and bi-[8]annulenylyene anion radical is formed, further exposure of the solution to the metal causes the EPR spectrum of (C₈H₆)₂^{•-} to fade (presumably due to reduction to the dianion) and the spectrum shown in Figure 1 grows in.

The spectrum (Figure 1) can be nicely simulated using coupling constants of 3.47, 3.085, 2.015, 1.06, 0.91, and 0.52 G, each splitting arising from a pair of hydrogens, which seems strange unless the odd electron is located predominately in one of the cyclooctatetraenyl moieties. B3LYP/6-31G* calculations performed on the anion radical of tri-[8]annulenylyene [(C₈H₆)₃^{•-}] suggest that (C₈H₆)₃^{•-} has a rather unusual conformation and that the odd electron is, indeed, predominantly localized in just one of the eight-membered ring systems. The ring system containing the odd electron is rendered

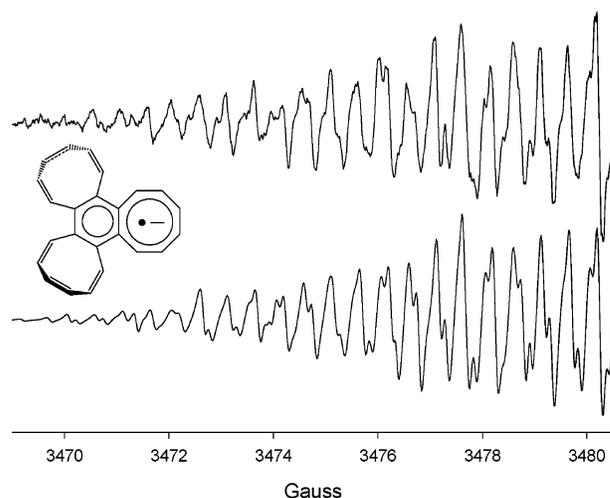
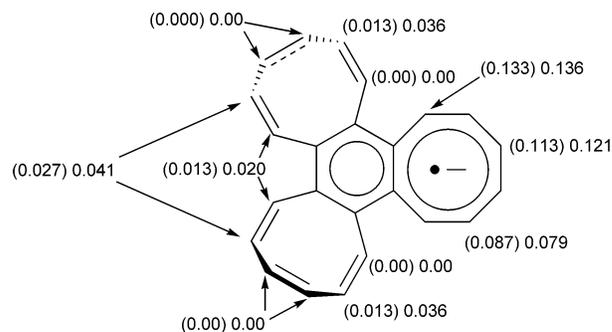


Figure 1. (Upper) Low-field half of the X-band EPR spectrum of the anion radical of tri-[8]annulenylyene in HMPA recorded at ambient temperature with a modulation amplitude of 0.1 G. (Lower) A computer-generated simulation using the coupling constants reported in text and a line width of 0.12 G. A small amount of *tert*-butoxycyclooctatetraene anion radical (5%), which is formed from the interaction of *tert*-butoxide with bromocyclooctatetraene, was included in the simulation.

nearly flat. The other two outer rings remain in opposed tublike conformations. No pair of eight-membered ring systems can be flat at the same time due to the steric crowding of the pseudo-ortho protons.

This type of calculation has shown remarkable success in predicting spin densities in the C₈H₆^{•-} and (C₈H₆)₂^{•-} systems.⁷ The B3LYP/6-31G*-predicted carbon p_z spin densities (shown in parentheses in structure 1) are in good agreement with the experimental spin densities (to the right) obtained from the *a*_H's and the McConnell relationship⁵ (*a*_H = *Qρ* with *Q* = 25.6 G).⁸



Quenching the anion radical solution that exhibited the EPR spectrum shown in Figure 1 with I₂ in pentane followed by high-vacuum distillation and chromatography on a silica gel column allowed for the isolation of a yellow oil. Pure (C₈H₆)₃ could be isolated via distillation of this oil. By the time the sample could be

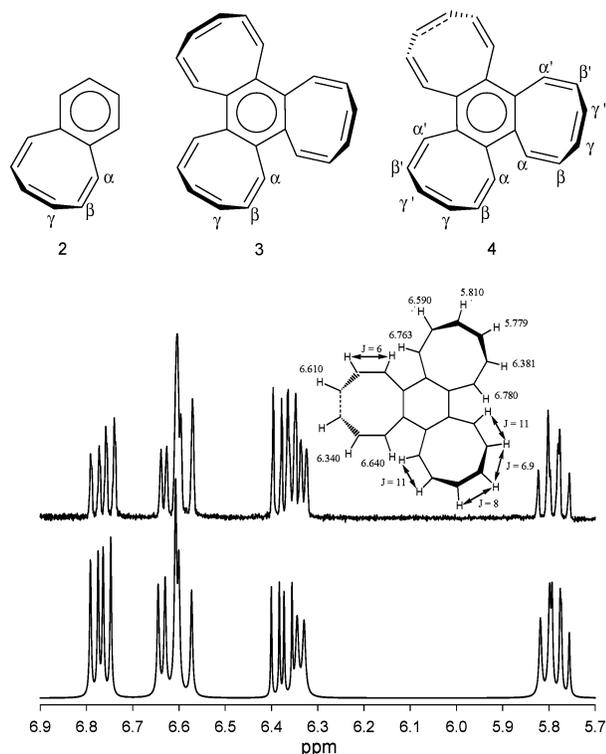


Figure 2. ^1H NMR spectrum (400 MHz) of the reoxidized solution that exhibited the EPR spectrum shown in Figure 1. The simulation (lower) was generated using the chemical shifts and the J couplings shown. Note that the α and α' protons are not equivalent, but fast ring-puckering dynamics render the two α protons magnetically equivalent.

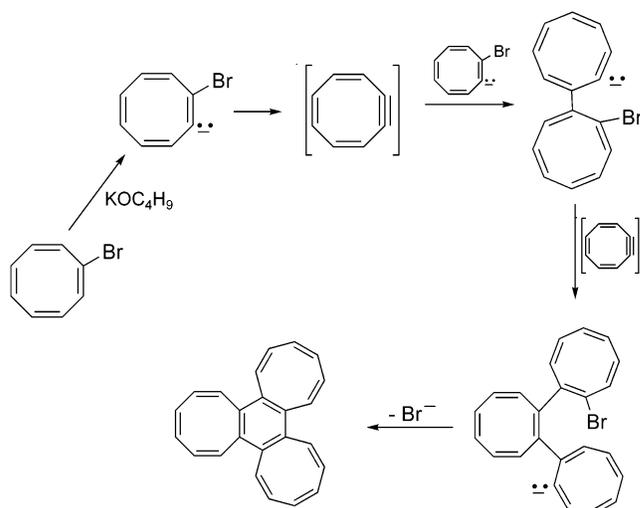
submitted to field desorption mass spectroscopy, most of it had polymerized. However, the mixture still exhibited a prominent parent peak at $m/e = 306$ with a strong $P + 1$ peak. The parent peak is the highest in magnitude for those peaks with $m/e \leq 306$, but heavier materials were also found in the spectrum, which reveals peaks from 355 to 590. Testifying to the fragility of the neutral material, we were unable to obtain the $m/e = 306$ peak on a GC-mass spectrometer. The tri-[8]annulenyne breaks down and/or polymerizes on the GC column.

Upon ^1H NMR analysis (Figure 2), benzo-[8]annulene (structure 2) reveals a singlet at δ 5.77 for the hydrogens at γ positions and a pair of doublets ($J = 10$ Hz) with chemical shifts of δ 5.92 and 6.47, and $J_{\beta\gamma} = 0.9$. Two conformers of tri-[8]annulenyne are possible. The conformer calculated to be of higher energy has all three external rings systems displaced above the plane of the benzene ring (structure 3). B3LYP/6-31G* calculations predict a conformer of lower energy, where two ring systems are bent above and one bent below the plane of the benzene ring (structure 4). If structure 3 represented the material "in hand," only three multiplets would be observed in the ^1H NMR spectrum. However, if structure 4 represents our material, then the α and α' protons on the ring systems above the plane are not equivalent. This is also the case for the β and β' and γ and γ' protons.

The dynamics of the neutral system, where the folded up and down rings interchange, are slow on the NMR time scale, and the dynamics of the anion radical where the electron "hops" from ring to ring are slow on the EPR time scale.

The $(\text{C}_8\text{H}_6)_3$ system forms under nearly identical conditions as does $(\text{C}_6\text{H}_4)_3$, and, presumably, the mechanisms are analogous (Scheme 1).¹ However, $(\text{C}_8\text{H}_6)_3$ is much more fragile than is the

Scheme 1



tri-[6]annulenyne system. This is due to the lack of aromatic character in the three outer rings of $(\text{C}_8\text{H}_6)_3$ and the steric crowding between the pseudo-ortho (α) ring protons, which cannot simultaneously occupy the same plane. The $(\text{C}_8\text{H}_6)_3$ system can, however, be stabilized via the addition of an extra electron (also known to stabilize the bi-[8]annulenyne system).⁷

These results suggest that a host of other triannulenylenes is possible, and their stabilities should be enhanced by the puckering of the larger ring systems to avoid steric crowding. Using just the well-known annulenes (up to [22]annulene),¹⁰ not including those with cyclobutadiene units, there are 165 possible members in this class of compounds, including the asymmetrical systems, e.g., $n \neq m \neq l$ in reaction 1. Only one has been known since 1867.

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Supporting Information Available: Experimental details and H-H COSY spectra (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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