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Benzocyclynes Adhere to Hückel's Rule by the Ring Current Criterion in Experiment (^{1}H NMR) and Theory (NICS)

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Abstract: The experimental ^{1}H NMR chemical shift values of six benzocyclynes (benzodehydroannulenes) have been assigned and, in combination with nucleus-independent chemical shift (NICS) calculations, shown to indicate diatropic behavior for $4n+2$, paratropic behavior for $4n$ π systems.

Keywords: Annulenes; Aromaticity; Cycloalkynes; NMR

Benzocyclynes (benzodehydroannulenes lacking alkenyl ring carbons) [1] have experienced a recent renaissance [2] because of their topology and highly energetic functionality. There has been considerable controversy over whether such systems, when planar, adhere to Hückel's rule and hence show aromatic/antiaromatic behavior, since the latter, if present, would be greatly attenuated compared to the core annulene systems by virtue of the perturbing nature of the fused benzene rings, the incorporation of triple bonds, and, for the larger members, ring size [3]. During the course of our studies aimed at the conversion of members of this class of compounds to novel materials [4], we noted distinct, if weak, diatropicity in compound **5** [4a] (Figure 1) prompting the present study.

A literature search revealed only [5] six parent benzocyclynes **2-7** which were unambiguously planar and sufficiently characterized to be useful for our purposes. The smallest one, **2**, was deemed paratropic [6a] (hence antiaromatic by the ring current criterion [3]), albeit with the caveat of the imponderableness of ring strain and triple bond anisotropy [6b]. In contrast, benzocyclynes **3** [7a] and **4** [8a] were the subject of incongruous assessments [7b,8b-d], including inadequate chemical shift calculations [9]. No comment was made on the potential paratropicity in **6** [10], but **7** was regarded as weakly diatropic [11]. Except for **2** [6b] and **5** [4a], the proton chemical shifts H_α and H_β of these molecules, including those in reference structure **1**, had not been assigned, thus obviating any meaningful correlations.

In order to shed light on this problem, the missing δ values were obtained by HMBC [12] and confirmed by T1 measurements, with the exception of those of **7** which could be readily assigned by comparison to the ^{1}H NMR data of β-alkylated analogs [13]. The suitability of **1** as an

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atropic substructure appears justified, as the magnetic effects of the added (phenyl and/or alkynyl) substitution [14] and (potential) strain [15] in **2**-**7** seem negligible. Inspection of the data, especially of $\delta_{H\alpha}$ in comparable structural environments, reveals a distinct, albeit relatively subtle, alternation in accord with Hückel's rule, with **2**, **3**, **4**, and **6** as para-, **5** and **7** as diatropic.

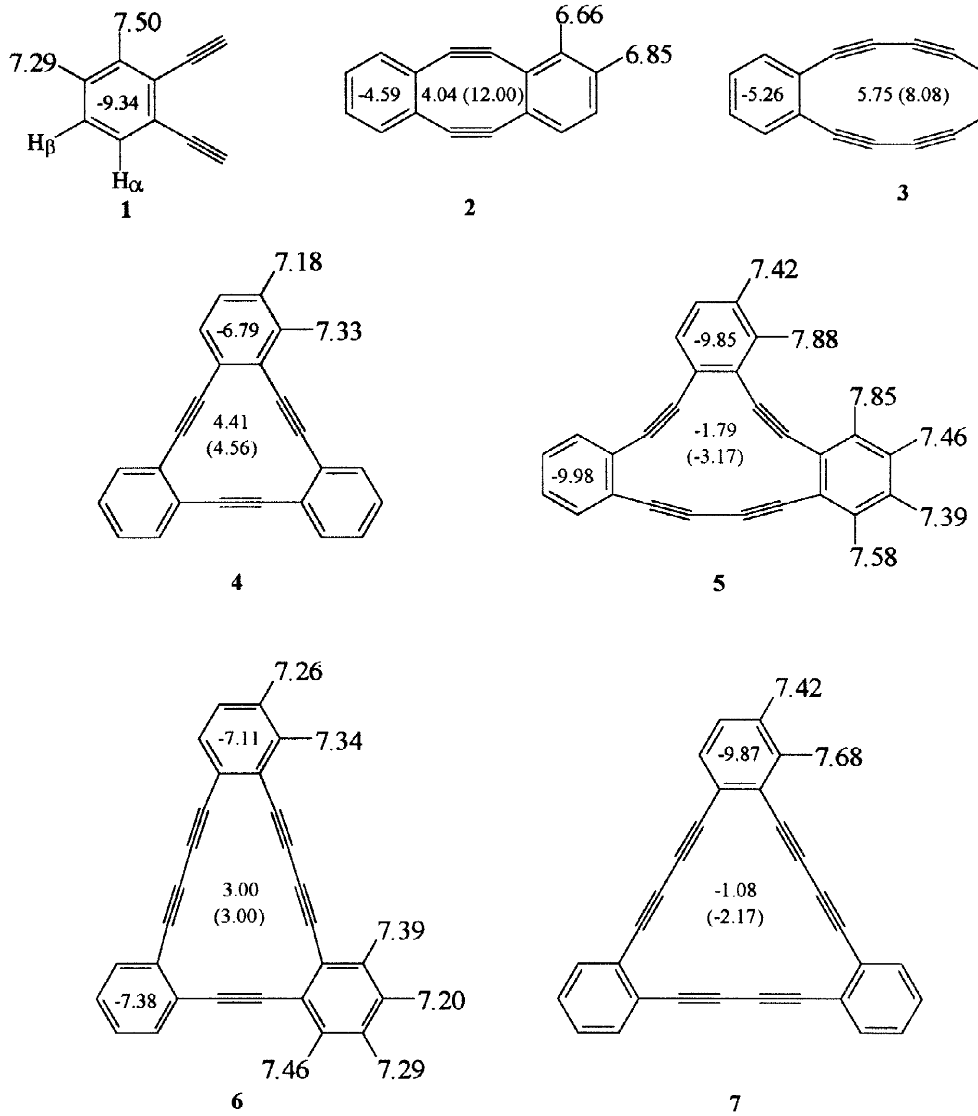

Figure 1. Measured (periphery ppm) and NICS (inside rings, corrected data in parentheses) values for **1**-**7**.

Moreover, the magnitude of these effects seems to decrease with increasing ring size (**2** vs. **3**, **4** vs. **6**, and, arguably, **5** vs. **7**) and number of fused benzene nuclei (**3** vs. **4**), as expected [3].

Encouraged by these trends, theoretical confirmation was sought by employing Schleyer's nucleus-independent chemical shift (NICS) method (Figure 1) [16]. Gratifyingly, initial calculations reveal perfect agreement between the sign of the NICS and the electron count of the cyclyne. We next turned to the problem of local anisotropy, particularly of the alkyne units [17]. For this purpose, the ring current contribution to the NICS was "turned off" in **2**-**7** by replacing one benzene (for **5** and **6** the top ring in Figure 1) with an ethano bridge, maintaining planar geometry and maximum symmetry. The resulting NICS values were then subtracted from the initial data to provide the "corrected" number in Figure 1. It is evident that the trend of alternating para- and diatropicity is not only still present, but indeed reinforced. Moreover, the attenuating effects of increasing ring size and benzofusion are clearly evident, and qualitative agreement between the magnitude of the NICS and the measured NMR data is apparent. It is also noteworthy that the NICS values of the fused benzenes are indicative of increased diatropicity when fusion is to a 4n+2, decreased diatropicity when it is to a 4n π cycle, consistent with expectation [1,3]. Finally (Figure 2), the success of the methodology encourages us to predict that unknown **8** will be strongly diatropic and **9**, known to be nonplanar and atropic [18] (confirmed by NICS), will become paratropic on planarization.

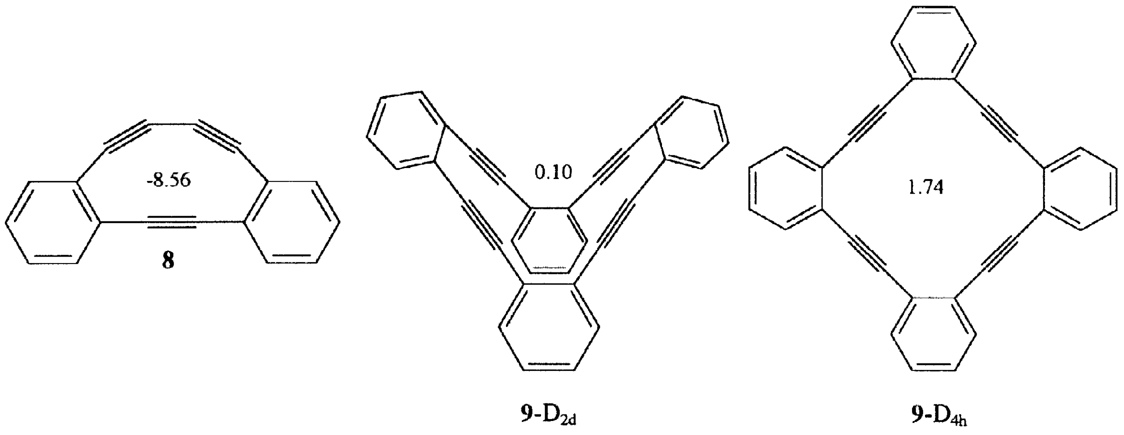

Figure 2. Corrected NICS values for **8** and two geometries of **9**.

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