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[5]Pericyclynes Are Not Homoaromatic

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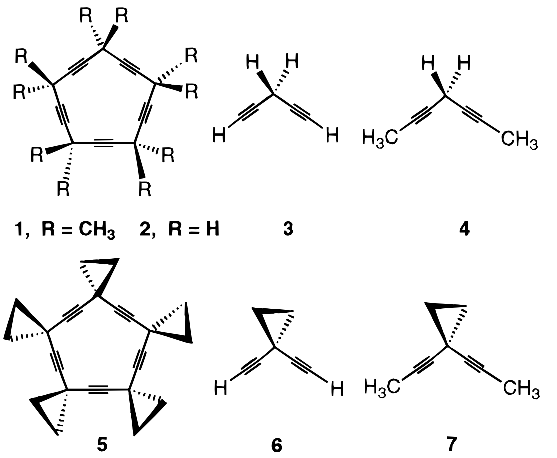
[5]Pericyclynes were investigated at high ab initio and density functional levels. On the basis of the geometric, energetic, and magnetic criteria of aromaticity, [5]pericyclynes are not homoaromatic despite their intriguing structure. The strain energy of [5]pericyclynes is negligible.

In 1983, Scott *et al.*[1] synthesized decamethyl[5]pericyclyne (**1**, R = CH_3) and reported strong electronic interactions among the five acetylenic units by photoelectron and electron transmission spectroscopy.[2] These interactions were ascribed to the possible cyclic homoconjugation, i.e. homoaromaticity. Furthermore, on the basis of the average heat of hydrogenation in the series of acyclic alkynes $[R_3C(C{\equiv}CCR_2)_nR$, R = CH_3, $n = 2{-}5]$ and correction for strain, Scott *et al.* claimed that **1** has an aromatic stabilization energy (ASE) of 6 kcal/mol.[3] However, this conclusion not only depends on the accuracy of the experimental determination, but also on the manner in which the heats of hydrogenation are evaluated.[4] For example, when the difference of the heat of hydrogenation between $n = 4$ and $n = 5$ is used as the basis, instead of the average heat of hydrogenation from $n = 2{-}5$, **1** is indicated to be destabilized by 3 kcal/mol only.[4a]

An ab initio (HF/3-21G) study on the parent system also found **2** (R = H) to be destabilized, but only by 1 kcal/mol. It was concluded that "the magnitude of the aromatic stabilization, whether positive or negative, is probably not large, and the accuracy of the methods used, either theoretical or experimental or both, is insufficient to fix the quantity more accurately".[4a] MNDO calculations suggested that interactions between triple bonds are hyperconjugative in the π system and homoconjugative in the σ system.[4b]

This communication reports a comprehensive theoretical investigation of the possible homoaromatic character of **2** and **5** based on the geometric, energetic, and magnetic criteria of aromaticity.[5] Geometry optimizations (Becke3LYP/6-31G*) and single-point energy computations (Becke3LYP/D95(d)//Becke3LYP/6-31G*) were carried out with density functional theory (DFT) using the Gaussian 94 program package.[6] Magnetic properties were calculated using the IGLO (individual gauge for localized orbitals) method employing the DZ basis set and Becke3LYP/6-31G* geometries.[7] All data are summarized in Table 1.

Scheme 1



The D_{5h} symmetric **2** is an energy minimum at Becke3LYP/6-31G*. As shown in Figure 1, the C≡C triple (1.207 Å) and C−C single (1.471 Å) bond lengths in **2** are nearly the same as in 2-butyne (1.209 and 1.462 Å), in 1,4-pentadiyne **3** (1.206 and 1.469 Å), and in 2,5-heptadiyne **4** (1.208 and 1.471 Å) reference structures. The $\equiv C{-}CH_2{-}C\equiv$ angle (112.2°) and the 1,3 $\equiv C{\cdots}C\equiv$ separation (2.441 Å) in **2** differ only slightly from those in **3** (113.7° and 2.460 Å) and in **4** (113.8° and 2.465 Å). Hence, there is no geometric evidence for homoconjugation, since aromatic compounds should show evidence for some bond length equalization due to cyclic delocaliza-

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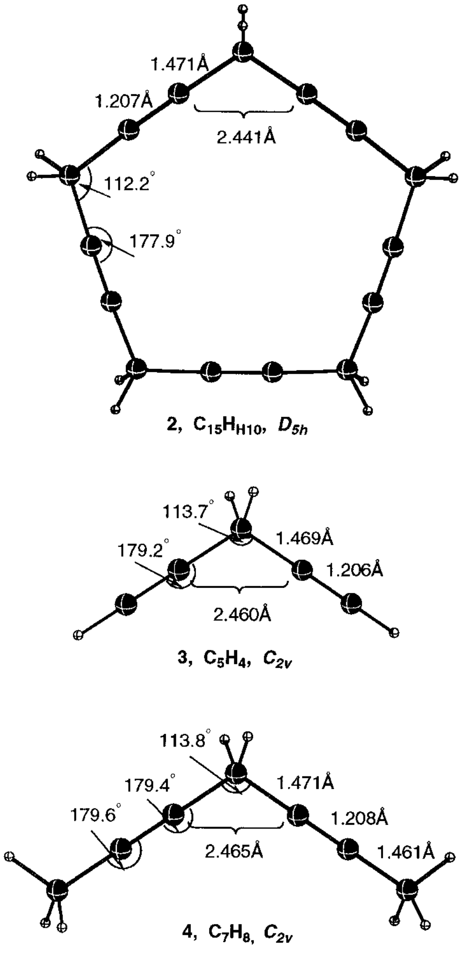
Table 1. Calculated Total Energies (E_{tot}, Hartree) for 2–7 and Magnetic Susceptibilities (χ_{tot}, ppm cgs) at IGLO/DZ//Becke3LYP/6-31G*

no.	E_{tot}[a]	E_{tot}[b]	χ_{tot}
2	−577.27962[c]	−577.32235	−175.7
3	−192.78288	−192.79960	−60.2
	−192.78267[d]	−192.79933[d]	
4	−271.43553	−271.45628	−90.7
	−271.43536[d]	−271.45606[d]	
5	−964.22137	−964.29854	–
6	−270.17226	−270.19513	–
	−270.17190[e]	−270.19495[e]	
7	−348.82434	−348.85167	–
	−348.82394[e]	−348.85137[e]	
H−C≡C−H	−77.32565	−77.33222	−25.3
$H_3C-C\equiv C-CH_3$	−155.97896	−155.99102	−55.8

[a] At Becke3LYP/6-31G*. [b] At Becke3LYP/D95(d) using the Becke3LYP/6-31G* geometries. [c] At Becke3LYP/6-31G* **2** is an energy minimum (NIMAG = 0, ZPE = 120.1 kcal/mol). [d] Strain correction using the same angles as in **2**. [e] Strain correction with the same angles as in **5**.



2, $C_{15}H_{H10}$, D_{5h}

3, C_5H_4, C_{2v}

4, C_7H_8, C_{2v}

Figure 1. Becke3LYP/6-31G* optimized geometries for **2**–**4**.

tion. While **2** is not aromatic geometrically, this is not a very sensitive criterion.

The aromatic stabilization energy (ASE) estimates using the homodesmotic reactions (eqs 1 and 2) employed *angle strain corrected* 1,4-pentadiyne (**3**) and 2,5-heptadiyne (**4**) and acetylene as well as 2-butyne reference molecules. That is, the angles of the reference molecules were set at the same values as in **2**. This refinement is modest. The calculated strain energy for **2** is only 0.7–0.9 kcal/mol. The computed ASE at Becke3LYP/D95(d) using the Becke3LYP/6-31G* geometries of 8.2 kcal/mol (eq 1) indicates a small destabilization in agreement with the HF/3-21G result.[4a] Using homodesmotic eq 2, the calculated ASE of 1.8 kcal/mol is negligibly small. This indicates that the evaluation of ASE depends on the reference molecules used, and reference **4** is more appropriate than **3**, since the triple bond in **2** is connected with two tetravalent carbon atoms as in **4**. When compared with the aromatic stabilization for benzene (−21.7 kcal/mol) and the antiaromatic destabilization for cyclobutadiene (36.3 kcal/mol),[5b] **2** is not aromatic energetically.

$$5(\mathbf{3} - \text{H}{-}\text{C}{\equiv}\text{C}{-}\text{H}) = \mathbf{2} \qquad \text{(eq 1)}$$

$$\text{ASE } (\mathbf{2}) = 8.2 \text{ kcal/mol and } \Lambda\ (\mathbf{2}) = -1.2$$

$$5(\mathbf{4} - \text{H}_3\text{C}{-}\text{C}{\equiv}\text{C}{-}\text{CH}_3) = \mathbf{2} \qquad \text{(eq 2)}$$

$$\text{ASE } (\mathbf{2}) = 1.8 \text{ kcal/mol and } \Lambda\ (\mathbf{2}) = -1.2$$

In addition to the geometric and energetic criteria, the magnetic susceptibility exaltation (Λ) due to the presence of cyclic electron delocalization (ring currents) provides a highly important evidence for aromaticity.[5,8] Generally, Λ is defined as the difference between the bulk magnetic susceptibility (χ_M) of a compound and the susceptibility (χ_M') estimated from an increment system for the same structure without cyclic delocalization ($\Lambda = \chi_M - \chi_M'$).[8] In this paper, Λ is derived from the homodesmotic equations 1 and 2 using IGLO data.

At IGLO/DZ//Becke3LYP/6-31G*, the calculated magnetic susceptibility exaltation for **2**, −1.2 ppm cgs both from eqs 1 and 2 (in contrast to ASE, which depends on the choice of reference molecules), is negligibly small for such a large system with ten in-plane and ten out-of-plane π electrons. The value for the ten π-electron naphthalene is −28.2.[9] Hence, **2** is neither aromatic nor antiaromatic.

^{7}Li chemical shifts are a useful probe of ring current effects in organolithium compounds.[10,11] Li cations complexed to the π-faces of aromatic systems are shifted upfield due to cyclic electron delocalization; for example, the calculated δ $^7Li^+$ is −6.9 ppm in cyclopentadienyl lithium (CpLi).[10] The calculated δ ^{7}Li of Li^+ in the ring center of **2** is only −1.7 ppm; this is in the normal range of ±2 ppm, e.g. −1.5 ppm in the *cis*-1,3-butadiene−Li^+ complex.[10] Thus, **2** is nonaromatic based on the geometric, energetic, and magnetic criteria of aromaticity and it is not homoconjugated.

Extended perspirocyclopropanated [*n*]pericyclynes have been characterized experimentally recently.[12–14] Cyclopropane rings are well known to be better potential π

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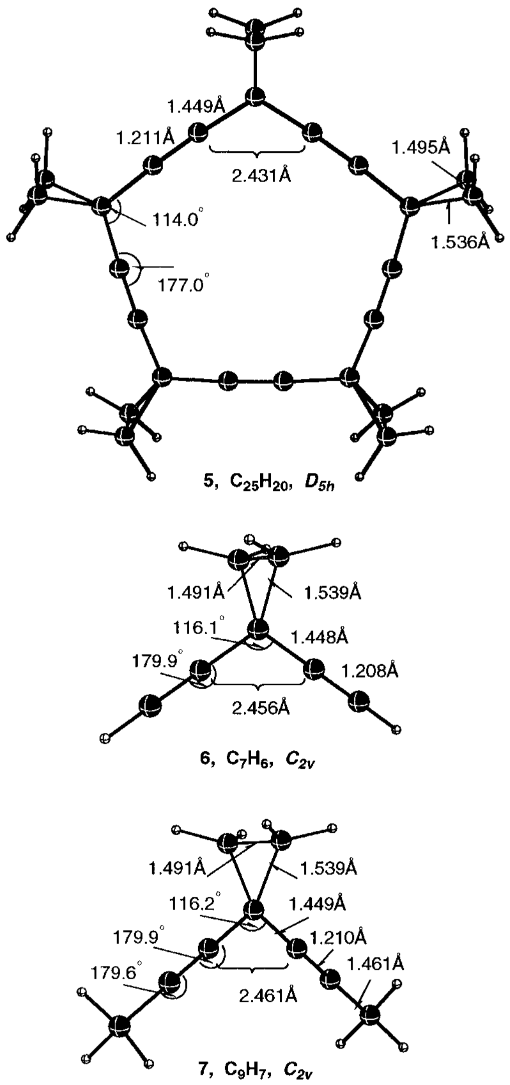

Figure 2. Becke3LYP/6-31G* optimized geometries for **5**−**7**.

donors than methyl groups. Hence, we optimized the geometries (Becke3LYP/6-31G*) of pentaspirocyclopropane [5]pericyclyne (**5**), 1,1-diethynylcyclopropane (**6**), and 1,1-dipropynylcyclopropane (**7**) reference structures shown in Figure 2. The C≡C triple and single bonds (1.211 and 1.449 Å) in **5** have nearly exactly the same lengths as in **6** (1.208 and 1.448 Å) and in **7** (1.210 and 1.449 Å). Thus, no tendency toward bond length equalization is present in **5**. The 1,3 ≡C····C≡ separation (2.431 Å) and ≡C−CH_2−C≡ angle (114.0°) in **5** are slightly shorter and smaller than those in **6** (2.456 Å and 116.1°) and in **7** (2.461 Å and 116.2°).

Compared with **2**, the triple bond is longer and the single bond is shorter in **5**. The 1,3 ≡C····C≡ separation in **5** is less than in **2**, but the *corresponding bond angle* is larger. These effects due to the cyclopropane ring are in agreement with the experimental observations on the corresponding extended system[13] and also are found in the two sets of reference structures, **3** and **6**, as well as **4** and **7**.

$$5(\mathbf{6} - \mathrm{H{-}C{\equiv}C{-}H}) = \mathbf{5} \qquad \text{(eq 3)}$$

$$\mathrm{ASE}\ (\mathbf{5}) = 9.5\ \mathrm{kcal/mol}$$

$$5(\mathbf{7} - \mathrm{H_3C{-}C{\equiv}C{-}CH_3}) = \mathbf{5} \qquad \text{(eq 4)}$$

$$\mathrm{ASE}\ (\mathbf{5}) = 2.0\ \mathrm{kcal/mol}$$

Based on homodesmotic eq 3, **5** is destabilized by 9.5 kcal/mol. However, this evaluation depends on the choice of reference structures. Indeed, using homodesmotic eq 4 with the more appropriate reference molecule **7**, the ASE for **5** is only 2.0 kcal/mol (Becke3LYP/D95(d)//Becke3LYP/6-31G*). Thus, **5**, just like **2**, is not homoaromatic based on the geometric and energetic criteria. Relative to **6** and **7**, the calculated strain energy for **5** is negligible, ca. 0.6−0.9 kcal/mol.

In conclusion, [5]pericyclynes **2** and **5** are not homoaromatic based on the geometric, energetic, and magnetic criteria. Neither **2** nor **5** exhibit any bond length equalization, nor any significant aromatic stabilization energies (ASE). They are essentially strain free. The nonhomoaromaticity of **2** is also shown by the negligible magnetic susceptibility exaltation ($\Lambda = -1.2$) and by the normal δ ^{7}Li (−1.7 ppm) of Li^+ placed in the center of the molecule. The calculated magnetic susceptibility exaltation has the advantage of being independent of the choice of reference molecules, in contrast to the aromatic stabilization energy evaluation. Despite their intriguing structures, neither **2** nor **5** have exceptional ground state properties.

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