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From Dodecahedrapentaene to the “[*n*]Trannulenes”. A New In-Plane Aromatic Family

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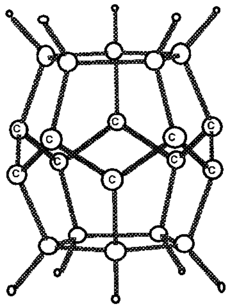
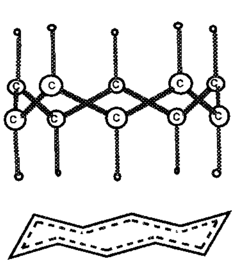
Hückel ($4n + 2$) π-electron annulenes comprise the most basic family of aromatic compounds.[1] In their idealized structures, all the p-orbitals are perpendicular to the ring planes. However, angle strain and steric effects result in a variety of configurational preferences and may even preclude planar arrangements.[1,2] We now present computational results on a new class of $(CH)_n$ Hückel annulenes which have uniform shapes, zigzag (trans) carbon rings, and inward-pointing p-orbitals. These “trannulenes” extend the concept of aromaticity and antiaromaticity to unconventional topologies.

Based on MNDO-CI calculations, McEwen and Schleyer[3] predicted that the delocalized [10]annulene subunit in dodecahedrapentaene (**1**) should be aromatic; the overlap of adjacent p-orbitals results in “in-plane“ cyclic delocalization (in-plane aromaticity).[4] Beside confirming this predication at higher levels of theory,[5] we now demonstrate the exciting possibility that the *all-trans*-cyclodecapentaene (**2**), the central unit in **1**[6a,e] also could be the first member of a new *all-trans*-[*n*]annulene family with in-plane conjugation, the [*n*]trannulenes. Indeed, somewhat similar in-plane conjugation is present in [*n*]cyclacenes[6] and in nanotubes,[7] although these are composed of intact benzenoid units. The computed geometries, energies, and magnetic properties show that the [*n*]trannulenes follow the Hückel rule perfectly: the $4n + 2$ electron species are aromatic, while the singlets with $4n$ electrons are antiaromatic.



1, D_{5d}



2, D_{5d}

At HF/3-21G and B3LYP/6-31G*, **1** is a minimum (NIMAG = 0) in D_{5d} symmetry, i.e., all the central C−C bonds have the same length (1.400 Å vs 1.396 Å for benzene). Hence, **1** is aromatic geometrically.[8] The calculated stabilization energy (−11.3 kcal/mol) supports the earlier conclusion[1] that substantial stabilization results from the aromaticity in **1**. The NICS (nucleus-independent chemical shift)[9] of −16.5 ppm calculated at the geometric center, is comparable with NICS = −17.3 for the planar D_{10h} [10]annulene[10] and NICS −15.2 for benzene at the CSGT/B3LYP level. Therefore, **1** is aromatic based on the geometric, energetic and magnetic criteria.[11]

The parent [10]trannulene (**2**), with center-oriented p-orbitals, is aromatic as well. While **2** has one imaginary frequency (NIMAG = 1) at HF/6-31G* (-109 cm^{-1}) in D_{5d} symmetry, this form is a minimum (NIMAG = 0) at B3LYP/6-31G* with equal C−C lengths (1.412 Å). Electron correlation is known to be important for delocalized systems.[12] The same situation holds for the higher aromatic [*n*]trannulene homologues (n = 14, 18, 22, and 26). These have D_{md} ($m = n/2$) symmetry minima only at B3LYP/6-31G* (Table 1). All the aromatic trannulenes are considerably higher in energy than their annulene counterparts,[13] e.g., 57.6 kcal/mol for $C_{14}H_{14}$ (C_2) and even 23.7 kcal/mol for $C_{30}H_{30}$ (D_{3h}) (Table 1). These energy differences reflect the additional strain in trannulenes.

The D_{md} C−C bond lengths decrease from [10]trannulene **2** (C−C = 1.412 Å, CCC = 115.3°, CCCC = 109.5°) continuously to 1.397 Å in D_{15d} [30]trannulene; the CCC bond angles converge to ca. 123°, and the CCCC dihedral angles become larger due to the increase in the ring size. The strain decreases as a result. Larger [*n*]annulenes are known to favor localized geometries.[13] For trannulenes, bond alternation is found even for $C_{10}H_{10}$ at HF/6-31G*,[6a] but first sets in for the D_{15} $C_{30}H_{30}$ minimum at B3LYP/6-31G* (r_{cc} = 1.398, 1.408 Å; cf. D_{17} $C_{34}H_{34}$ r_{cc} = 1.381, 1.413 Å).

Both the calculated χ and Λ evaluated from acyclic models increase dramatically due to the dependence of magnetic susceptibility on the square of the ring area,[14] but the NICS values become nearly constant (Table 1). This shows the advantage of

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Table 1. B3LYP/6-31G* Computed Geometries, Energies, and Magnetic Properties (CSGT) of [*n*]Trannulenes

formula	PG	C−C (Å)	CCC (deg)	CCCC (deg)	χ	Λ	NICS[a]	δ ^{1}H[b]	E_{rel}[c]	$\Delta H_f°$[d]	$\Delta H_f°/n$
$C_{10}H_{10}$	D_{5d}	1.412	115.3	109.5	−78.3	−29.3	−14.0	2.0		183.2	18.3
$C_{12}H_{12}^{2+}$	D_{6d}	1.401	115.2	122.2	−102.2	−61.5	−17.0	4.5			
$C_{12}H_{12}^{2-}$	D_{6d}	1.423	120.9	116.7	−138.4	−64.3	−14.3	1.0			
$C_{14}H_{14}$	D_{7d}	1.404	119.5	127.6	−174.4	−105.8	−17.2	1.8	57.6	170.0	12.1
$C_{14}H_{14}$[e]	D_7	1.346, 1.453	119.3	127.2, 128.4	−145.7	−77.1	−12.0	2.5			
$C_{18}H_{18}$	D_9d	1.401	121.4	138.4	−320.7	−232.5	−17.9	1.0	49.1	174.3	9.7
$C_{18}H_{18}$[e]	D_9	1.339, 1.457	121.1	139.1, 138.1	−211.9	−123.7	−8.9	2.7			
$C_{22}H_{22}$	$D_{11}d$	1.399	122.4	145.6	−534.7	−426.9	−17.9	0.4	37.7	186.3	8.5
$C_{26}H_{26}$	$D_{13}d$	1.398	123.0	150.7	−832.4	−705.0	−17.8	−0.1	29.6	200.3	7.7
$C_{30}H_{30}$	$D_{15}d$	1.397	123.4	154.5	−1229.3	−1082.3	−17.8	−0.5	23.7	220.3	7.3
$C_{12}H_{12}$	D_6	1.363, 1.468	117.8	119.2, 120.5	54.9	113.7	35.7	10.6		196.5	16.4
$C_{16}H_{16}$	D_8	1.364, 1.451	120.6	133.1, 134.2	142.9	221.3	27.8	10.7		187.2	11.7
$C_{20}H_{20}$	D_{10}	1.365, 1.442	121.9	142.1, 142.7	251.9	349.0	21.6	10.3		191.2	9.6
$C_{24}H_{24}$	D_{12}	1.366, 1.437	122.7	148.6, 148.2	369.8	487.4	17.0	9.8		202.2	8.4
$C_{28}H_{28}$	D_{14}	1.367, 1.434	123.2	153.0, 152.6	482.4	619.6	13.4	9.1		216.8	7.7
$C_{12}H_{12}$ (3)[f]	D_{6d}	1.412	118.0	119.7	−118.4	−58.9	−15.3	2.7	5.1[g]	201.6	16.8
$C_{16}H_{16}$ (3)[f]	D_{8d}	1.405	120.7	133.6	−236.6	−157.4	−17.2	1.5	5.9[g]	193.1	12.1
$C_{20}H_{20}$ (3)[f]	$D_{10}d$	1.401	122.0	142.4	−414.3	−315.6	−17.6	0.6	6.4[g]	197.6	9.9
$C_{24}H_{24}$ (3)[f]	$D_{12}d$	1.400	122.8	148.4	−667.2	−548.9	−17.7	0.2	6.7[g]	208.8	8.7
$C_{28}H_{28}$ (3)[f]	$D_{14}d$	1.399	123.2	152.8	−1012.8	−874.9	−17.7	−0.1	7.3[g]	224.1	8.0

[a] NICS (ppm) at the geometric midpoint. [b] Relative to tetramethylsilane (σ $^1H_{TMS}$ = 31.0 ppm). [c] Energies relative to (4*n* + 2) electron annulenes: $C_{14}H_{14}$ (C_2), $C_{18}H_{18}$ (D_{6h}), $C_{22}H_{22}$ (C_{2v}), $C_{26}H_{26}$ (C_{2v}), and $C_{30}H_{30}$ (D_{3h}). [d] Estimated heats of formation (kcal/mol) based on $(CH)_n = (n/6)\ C_6H_6$ and the experimental heat of formation of benzene. [e] HF/6-31G* geometries were used. [f] Triplet states. [g] Singlet−triplet energy differences (kcal/mol) for the 4*n* electron trannulenes.

NICS over diamagnetic susceptibility exaltations (Λ)[11a,15] for quantitative comparisons of ring systems of different sizes. All the data in Table 1 reveal the aromatic character of the Hückel (4*n* + 2) [*n*]trannulenes. Both the NICS and Λ values computed with the HF/6-31G* D_m geometries of $C_{14}H_{14}$ and $C_{18}H_{18}$ show a reduction but not an elimination of aromatic character due to bond alternation.

^{1}H NMR chemical shifts are the most widely used criteria of aromaticity, especially for the large annulenes.[13,16] The computed δ ^{1}H for the D_{10h} [10]annulene is downfield (9.5 ppm) but is upfield (2.0 ppm) for [10]trannulene because of the perpendicular orientation of the hydrogens in the diatropically shielded region over the ring faces.

The antiaromatic 4*n* electron singlet [*n*]trannulenes behave quite differently.[17] For example, the [12]trannulene energy minimum has D_6 symmetry (NIMAG = 0 at B3LYP/6-31G*) and the C−C bond lengths alternate strongly (1.363 vs 1.468 Å), the susceptibility exaltation is paramagnetic (Λ = 113.7, with *n* = 12), and the NICS value (35.7 ppm) is highly positive. These properties are in sharp contrast to those of the corresponding 10-electron aromatic [12]trannulene dication (Λ = −61.0; NICS = −17.0) and the 14-electron aromatic [12]trannulene dianion (Λ = −74.0; NICS = −14.3). In addition, the δ ^{1}H's are upfield for these charged aromatic systems, but are downfield for [12]trannulene (Table 1). The other singlet 4*n* trannulenes (*n* = 16, 20, 24, and 28), with positive Λ, positive NICS, and downfield δ ^{1}H's, also are antiaromatic. The calculated Λ's increase dramatically, but the NICS values decrease as the ring size increases.

We confirmed recently that the triplet states of 4N−π-electron annulenes are aromatic rather than antiaromatic,[18] based on geometric, energetic, and magnetic criteria. Likewise the triplet states of the 4*n*-electron [*n*]trannulenes (*n* = 12, 16, 20, 24, and 28, D_{md} symmetry; *m* = *n*/2) have equal C−C bond lengths and are only 5.1 to 7.3 kcal/mol higher in energy than the corresponding singlet states (Table 1). These small singlet−triplet energy gaps reflect the considerable aromatic stabilization of the triplet states, since, for comparison, triplet naphthalene is 62.3 kcal/mol less stable at B3LYP than the singlet. The single C−C bond length (1.399 Å) of triplet [28]trannulene (D_{14d}) contrasts strongly with the bond length alternation of the singlet state (1.367 and 1.434 Å). In addition, the [28]trannulene triplet state also has negative NICS (−17.7) and Λ (−874.9); the δ ^{1}H is −0.1 ppm. The opposite features are found for the antiaromatic singlet states of [28]trannulene (Λ = 616.9, NICS = 13.4 and δ ^{1}H = 9.1). The other 4*n* triplet trannulenes show the same behavior. The heats of formation per each CH group of both aromatic and antiaromatic trannulenes decrease with the increase of the ring size, and should converge to ca. 7.0 kcal/mol with *n*'s larger than 30.

The trannulene family invites experimental realization and exploration.[19] Although higher in energy than the corresponding annulenes, the trannulenes have uniform configurations (D_n and D_{nd} symmetries) which facilitate direct comparisons, e.g. of structures, magnetic properties, and the onset of bond alternation. All of the [*n*]trannulenes follow the Hückel rule exactly: on the basis of geometric and magnetic criteria (magnetic susceptibility exaltations and NICS as well as proton NMR chemical shifts), the 4*n* + 2 electron singlets are aromatic, but the 4*n* singlets are antiaromatic. The triplet 4*n* electron trannulenes are aromatic based on the same criteria.

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Supporting Information Available: B3LYP/6-31G* total energies (hartrees) and geometries for [*n*]trannulenes and dodecahedraenes are summarized (25 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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