ORGANIC LETTERS

2011
Vol. 13, No. 14
3600–3603

[*n*]Imperilenes: Stacked [*n*]Trannulenes Separated by Planar Cycloalkane Rings

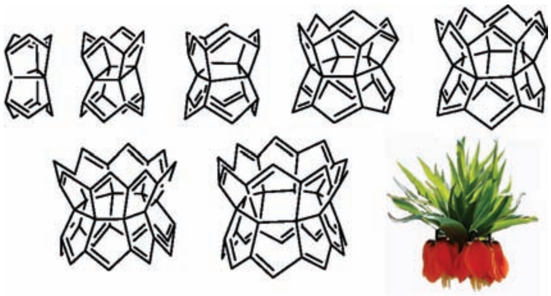
Farnaz A. Shakib,*,† Mohammad R. Momeni,† Judy I. Wu,‡ Paul von Ragué Schleyer,*,‡ Zahra Azizi,§ and Mehdi Ghambarian§

Department of Chemistry, Shahre-ray Branch, Islamic Azad University, Tehran 18155-144, Iran, Department of Chemistry, Center for Computational Chemistry, University of Georgia, Athens, Georgia 30602-2556, United States, and Department of Chemistry, Karaj Branch, Islamic Azad University, Karaj, 31485-313, Iran

fshakib@yahoo.com; schleyer@chem.uga.edu

Received May 7, 2011

ABSTRACT



Two trannulene moieties fused to each other by means of perfectly planar cycloalkane rings comprise an interesting class of molecules (above) named "*imperilenes*". Based on computed geometries and NICS$_{zz}$ values, only the [5], [7], and [9]imperilene singlet states as well as the $4+$ charged [4], [6], and [8]imperilenes and their higher energy neutral quintet states are aromatic. The π electron systems of the individual trannulene rings, rather than the overall electron count, determine the behavior.

Eaton et al.'s successful synthesis in 1972 of a dodecahedrane fragment made up of six fused pentagons, "[5]-peristylane" (Figure 1),[1] introduced a new family of polycyclic hydrocarbons. This has been augmented by the preparation of [3]- and [4]-peristylanes[2−5] as well as several aza, oxa, and thio heteroperistylanes.[6]

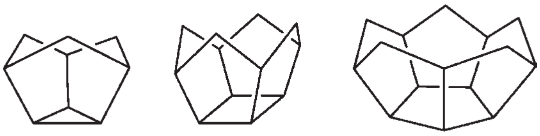


Figure 1. [3]-, [4]-, and [5]-peristylanes.

In 1986, McEwen and Schleyer considered unsaturated peristylapolyenes, with conjugated double bonds introduced around their perimeters,[7] in their theoretical examination of molecules exhibiting "in-plane aromaticity." They found that such [3]- and [5]-peristylenes (with $4n + 2$ π electrons) were aromatic but the $4n$ π electron [4]-peristylene was antiaromatic.

In 1998, Schleyer et al. focused on the all-trans-[*n*]-annulene perimeter subunits themselves. Their comprehensive

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† Shahre-ray Branch, Islamic Azad University.
‡ University of Georgia.
§ Karaj Branch, Islamic Azad University.

[1] (a) Eaton, P. E.; Mueller, R. H. *J. Am. Chem. Soc.* **1972**, *94*, 1014. (b) Eaton, P. E.; Mueller, R. H.; Carlson, G. R.; Cullison, D. A.; Cooper, G. F.; Chou, T.-C.; Krebs, E.-P. *J. Am. Chem. Soc.* **1977**, *99*, 2751. (c) Eaton, P. E.; A. Srikrishna, A.; Uggeri, F. *J. Org. Chem.* **1984**, *49*, 1728.

[2] Garratt, P. J.; White, J. F. *J. Org. Chem.* **1977**, *42*, 1733.

[3] Eaton, P. E.; Andrews, G. D.; Krebs, E.-P.; Kunai, A. *J. Org. Chem.* **1979**, *44*, 2824.

[4] Paquette, L. A.; Fischer, J. W.; Browne, A. R.; Doecke, C. W. *J. Am. Chem. Soc.* **1985**, *107*, 686.

[5] Mehta, G.; Gagliardini, V.; Schaefer, C.; Gleiter, R. *Org. Lett.* **2004**, *6*, 1617.

[6] (a) Mehta, G.; Vidya, R. *Tetrahedron Lett.* **1998**, *39*, 6403. (b) Sharma, P. K.; Jemmis, E. D.; Vidya, R.; Mehta, G. *J. Chem. Soc., Perkin Trans. 2* **1999**, 257. (c) Mehta, G.; Vidya, R.; Sharma, P. K.; Jemmise, E. D. *Tetrahedron Lett.* **2000**, *41*, 2999. (d) Mehta, G.; Vidya, R. *J. Org. Chem.* **2000**, *65*, 3497. (e) Mehta, G.; Vidya, R. *J. Org. Chem.* **2001**, *66*, 6913.

[7] McEwen, A. B.; Schleyer, P. v. R. *J. Org. Chem.* **1986**, *51*, 4357.

10.1021/ol201216d

Table 1. Principal Geometrical Parameters and Lowest Vibrational Frequencies ($\upsilon_{\min}$ in cm^{-1}) for Different Multiplicities (M, "s" Singlet, "t" Triplet, and "q" Quintet) of All the Optimized [*n*]Imperilenes ($n = 3-9$) at B3LYP/6-31G(d) as well as B3LYP/6-311++G(d,p) Calculated Relative Energies (E_{rel} in kcal/mol) and PW91/IGLO-III Calculated HOMO−LUMO Gaps (H−L in eV)

[*n*]	M	PG	CC(cyc)	CC(per)	CC(ver)	CCC(cyc)	$\upsilon_{\min}$	E_{rel}	H−L
[3]	s	D_{3h}	1.534	1.465	1.493	60.00	270.65	4.8	0.27
	t	C_{2v}	1.547, 1.564[a]	1.468, 1.549[b]	1.505,[a] 1.509	59.62, 60.76[c]	227.43	0.0	0.08[d] (0.44)
[4]	s[e]	D_{2d}	1.566	1.422,[f] 1.473[f]	1.498,[f] 1.526[f]	89.92	224.37	0.0	0.49
	t	D_{4h}	1.557	1.449	1.509	90.00	186.53	10.2	0.22 (0.44)
	q	D_{4h}	1.557	1.453	1.518	90.00	264.14	7.4	0.90 (2.10)
[5]	s	D_{5h}	1.532	1.421	1.516	108.88	234.00	0.0	2.72
	t	C_2	1.526−1.538	1.403−1.465	1.508−1.516	106.75−109.16	143.42	64.0	0.22 (0.11)
[6]	s	D_6	1.528	1.375,[g] 1.468	1.519	120.00	160.40	0.0	0.73
	t	D_{6h}	1.537	1.420	1.512	120.00	167.37	4.8	0.98 (0.35)
	q	D_{6h}	1.541	1.415	1.525	120.00	157.24	22.0	1.50 (2.23)
[7]	s	C_7	1.550	1.405	1.531	128.57	120.16	0.0	1.88
	t	C_1	1.547−1.555	1.374−1.454	1.519−1.531	128.41−128.69	18.22	36.5	0.49 (0.35)
[8]	s	C_8	1.579	1.369,[g] 1.435	1.538	135.00	85.83	9.5	0.82
	t	D_{4d}	1.584	1.403	1.527	135.00	94.56	0.0	1.44 (0.27)
	q	D_{4d}	1.592	1.399	1.539	135.00	82.23	35.3	0.82 (1.28)
[9]	s	D_{3h}	1.624	1.392	1.541	140.00	60.30	0.0	1.09
	t	C_s	1.620−1.624	1.375−1.416	1.528−1.542	140.00	25.14*i*	18.8	0.36

[a] Only one bond of each perimeter shows this different length. [b] Only two bonds of each perimeter show this different length. [c] Only one angle is different. [d] The gaps of higher states are given as alpha (beta). [e] Open-shell singlet. [f] Four bonds show this length. [g] Alternating bonds.

computational survey revealed that this "[*n*]trannulene" family with in-plane conjugation[8] involving "σ-type overlap of the π orbitals"[7] obeyed the Hückel rule and extended the concept of aromaticity and antiaromaticity to unconventional topologies. Since that time, many experimental examples of trannulene-containing systems have been reported.[9]

We now describe an elaborated peristylene family comprised of two trannulene units fused to opposite sides of an intervening *planar* [*n*]-membered cycloalkane ring. We name these intriguing species [*n*]imperilenes since they remind us of Crown Imperial flowers (*fritillaria imperialis*). This extension of in-plane (anti)aromaticity in parallel arrangements also affords opportunities to ascertain the consequence of a different type of ring stacking,[10] where the two trannulene rings are separated by a saturated ring, rather than being directly connected, as in cyclacenes.[11] A basic concern is the degree to which the two trannulene rings of the imperilenes interact, if they do so at all. The symmetric imperilene frameworks also force the intervening cycloalkane moieties to have planar conformations, quite rare for the larger rings.[12]

The structures were fully optimized at the B3LYP/6-31G(d) level as implemented in the Gaussian 03 program[13] and verified to be minima by harmonic frequency computations. HOMO−LUMO gaps and nucleus-independent chemical shift (NICS) indices[14,15] were computed at the PW91/IGLO-III//B3LYP/6-31G(d) level. The singlet and triplet states of all the structures as well as the quintet states of the [n = even]imperilenes were fully optimized as well. The [3]- and [8]imperilenes have triplet ground states 4.8 and 9.5 kcal/mol lower in energy than the corresponding singlets. All the other structures have singlet ground states (Table 1).

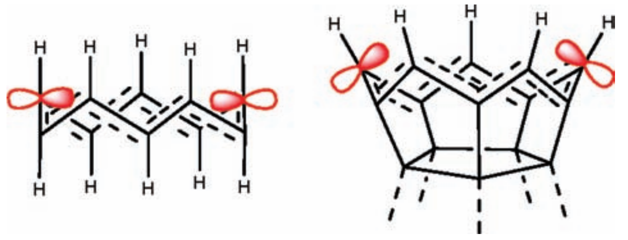

Figure 2. Horizontal inward-pointing *p*-orbitals of trannulenes (left) and tilted orbitals of imperilenes (right).

As implied by Figure 2, the double bond conjugation in the imperilenes differs somewhat from that in the trannulenes. However, the induced ring currents (and NICS values) are expected to be similar.

[n = Odd]Imperilenes. The singlet states of all [n = odd]imperilenes are aromatic (all have $4n + 2$ π electrons) and have equal perimeter bond lengths [CC(per), Table 1]

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(8) Fokin, A. A.; Jiao, H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1998**, *120*, 9364.

Table 2. Computed NICS_{zz} Values along the Inner C_n Axes of Different Ground State Multiplicities (M, "s" Singlet, "t" Triplet, and "q" Quintet) of [n]Imperilenes along with the 4+ Charged [n = Even]Imperilenes at GIAO-PW91/IGLOIII//B3LYP/6-31G(d) (n = 3–9)[a]

[n]	M	0 Å	0.5 Å	1.0 Å	1.5 Å	2 Å	2.5 Å	3 Å
[3]	s	−33.26	−24.88	−12.77	−3.53	−4.99	−6.45	−0.50
	t	−47.00	−36.12	−25.85	−14.93	−8.44	−13.74	−14.22
[4]	s	+54.39	+39.42	+26.47	+27.36	+24.86	+14.87	+7.28
	t	+69.83	+54.74	+44.83	+50.61	+47.52	+30.62	+16.01
	q	−35.96	−16.65	−3.57	−7.34	−8.07	−10.89	−10.86
	+4	+33.80[a]	+9.71[a]	−19.63	−32.92	−33.96	−27.13	−17.33
[5]	s	−0.80	−16.08	−38.52	−49.52	−48.93	−40.65	−30.03
	t[b]	+190.30	+191.52	+208.21	+232.42	+227.27	+183.33	+128.15
[6]	s	+84.55	+79.20	+73.21	+71.65	+66.67	+55.17	+41.22
	t[b]	+115.29	+110.99	+107.17	+106.27	+98.49	+81.25	+60.90
	q	−26.56	−35.54	−50.03	−57.28	−56.01	−48.67	−38.85
	+4	−23.03	−32.88	−48.97	−57.24	−56.27	−48.82	−38.78
[7]	s	−29.93	−36.92	−49.08	−55.91	−55.54	−49.92	−41.80
	t[b]	+139.69	+141.28	+138.62	+135.15	+125.89	+108.63	+87.20
[8]	s	+151.81	+148.26	+140.51	+131.28	+119.24	+103.46	+85.32
	t[b]	+132.55	+128.62	+120.53	+110.11	+98.20	+83.83	+68.47
	q	−46.06	−50.10	−57.71	−62.32	−61.64	−56.48	−48.80
	+4	−42.03	−46.56	−55.09	−60.43	−60.13	−55.13	−47.52
[9]	s	−45.85	−47.95	−52.06	−54.50	−53.62	−49.72	−43.96
	t[b,c]	+177.15	+174.05	+166.23	+155.41	+141.56	+124.64	+105.94

[a] Positive values are due to contributions from the σ-framework of the planar C_n ring. [b] The abnormally large paratropic NICS_{zz} values of these species are computational artifacts arising from their small H–L energy gaps. [c] Data for a triplet [9]imperilene transition state (NIMAG = 1, 25.14i cm^{-1}).

which decrease with ring size (as in the trannulenes)[8] from 1.465 Å in [3]imperilene to 1.392 Å in [9]imperilene. The central cycloalkane rings are planar, as dictated by symmetry. The [5, 7, and 9]imperilene singlet states are much more stable than the corresponding triplet states (by 64.0, 36.5, and 18.8 kcal/mol, respectively). The CC(per) bonds of the lower symmetry triplet [n = odd]imperilenes alternate in length.

Grids of NICS_{zz} values were computed, e.g., along the imperilene C_n axes (Table 2). All the singlet [n = odd] imperilenes with $4n + 2$ paired electrons have negative (diatropic) $\mathrm{NICS(0)}_{zz}$ values at the center. Figure 3 shows the diatropic (red dots, inside) and paratropic (green dots, outside) regions characterizing the magnetic aromaticity of the [n = odd]imperilene cages. The NICS_{zz} values for the n = 5, 7, and 9 singlet imperilenes (shown by the sizes of the dots) become more negative along the zz axis until the maximum magnitude is reached at about 1.5 Å away from the center. These positions are expected from the induced diatropic currents arising from inward-pointing p-orbitals (see Figure 2).

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(9) (a) Wei, X.-W.; Darwish, A. D.; Boltalina, O. V.; Hitchcock, P. B.; Taylor, R. *Angew. Chem., Int. Ed.* **2001**, *40*, 2989. (b) Troshin, P.; Lyobovskaya, R. N.; Ioffe, I. N.; Shustova, N. B.; Kemnitz, E.; Troyanov, S. I. *Angew. Chem., Int. Ed.* **2005**, *44*, 234. (c) Canteenwala, T.; Padmawar, P. A.; Chiang, L. Y. *J. Am. Chem. Soc.* **2005**, *127*, 26. (d) Tahara, K.; Tobe, Y. *Chem. Rev.* **2006**, *106*, 5274. (e) Also compare the pagodane dication: Drewello, T.; Fessner, W.-D.; Kos, A. J.; Lebrilla, C. B.; Prinzbach, H.; Schleyer, P.v.R.; Schwarz, H. *Chem. Ber.* **1988**, *121*, 187.

(10) (a) C. Corminboeuf, C.; Schleyer, P. v. R.; Warner, P. *Org. Lett.* **2007**, *9*, 3263. (b) Bean, D. E.; Fowler, P. W. *Org. Lett.* **2008**, *10*, 5573. (c) Aihara, J.-I. *J. Phys. Chem. A* **2009**, *113*, 7945.

(11) Choi, H. S.; Kim, K. S. *Angew. Chem., Int. Ed.* **1999**, *38*, 2256. Shansal, M. *Turk. J. Chem.* **2010**, *34*, 269.

(12) Dodziuk, H., Ed. *Strained Hydrocarbons Beyond the van't Hoff and Le Bel Hypothesis*; Wiley: 2009; ISBN-10: 3-527-31767-8.

(13) Frisch, M. J. et al. *Gaussian 03*; Gaussian, Inc.: Pittsburgh, PA, 2003 (full reference in Supporting Information).

(14) (a) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317. (b) Schleyer, P. v. R.; Jiao, H.; Hommes, N. J. R. v. E.; Malkin, V. G.; Malkina, O. *J. Am. Chem. Soc.* **1997**, *119*, 12669. (c) Chen, Z.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R. *Chem. Rev.* **2005**, *105*, 3842.

(15) (a) Corminboeuf, C.; Heine, T.; Seifert, G.; Schleyer, P. v. R. *Phys. Chem. Chem. Phys.* **2004**, *6*, 273. (b) Fallah-Bagher-Shaidaei, H.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R. *Org. Lett.* **2006**, *8*, 863. (c) Stanger, A. *J. Org. Chem.* **2006**, *71*, 883.

(16) (a) Corminboeuf, C.; Heine, T.; Seifert, G.; Schleyer, P. v. R.; Weber, J. *Phys. Chem. Chem. Phys.* **2004**, *6*, 273. (b) Heine, T.; Schleyer, P. v. R.; Corminboeuf, C.; Reviakine, R.; Seifert, G.; Weber, J. *J. Chem. Phys. A* **2003**, *107*, 6470.

(17) Also see: Gogonea, V.; Schleyer, P. v. R.; Schreiner, P. R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1945.

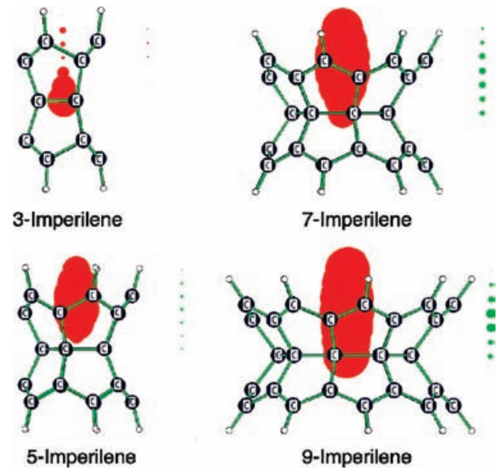

Figure 3. $NICS_{zz}$ grids for [*n*]Imperilenes (n = 3, 5, 7, and 9); red represents diatropic regions, and green, paratropic.

Although negative, the $NICS_{zz}$ values of [3]imperilene may not be reliable due to its very low HOMO−LUMO energy gap and the wave function instability of both the singlet and triplet states of this highly strained system. NICS values are often anomalous in such cases (e.g., for the triplet states in Table 2) and should not be used to evaluate aromaticity. Three-membered rings also are problematic.[16] The $NICS_{zz}$ progression of singlet [3]imperilene along the *zz* axis (Figure 3) does not resemble those of the [5, 7, and 9]imperilene, which are not in doubt. Molecular orbital (MO) analyses of the [n = odd]imperilenes reveal no interaction between the two trannulene moieties (see Figure S2, Supporting Information). The $NICS(2)_{zz}$ values (the NICS(2) point is roughly located at the individual trannulene moiety ring centers) of [5, 7, and 9]imperilene (−48.9, −55.5, and −53.6 ppm, respectively) also correspond nicely with the $NICS(0)_{zz}$ values for [10, 14, and 18]trannulene (−43.2, −50.3, and −51.9 ppm, respectively).

[*n* = Even]Imperilenes. Singlet [6 and 8]imperilenes have alternating perimeter bond lengths suggesting the absence of stabilizing electron delocalization. MO analyses for the singlet [n = even]imperilenes also reveal rather insignificant interactions between the two trannulene moieties (see Figure S2, Supporting Information).

The two different CC(per) lengths of singlet [4]imperilene do not alternate, but two longer bonds follow two shorter ones. The expectation based on Hückel theory that singlet [n = even]imperilenes should be antiaromatic is confirmed by their positive $NICS_{zz}$ values and grids showing powerful paratropic currents inside and diatropic currents outside (Table 2, Figure S1). Antiaromaticity also explains the very small singlet−triplet energy separation of [4 and 6]imperilene (7.8 and 4.8 kcal/mol, respectively) in contrast to [n = odd]imperilenes and the reversed singlet and triplet state stability of [8]imperilene.

Although triplet $4n$ π electron trannulenes are aromatic,[8,17] triplet [n = even] imperilenes are not since their MO's interact strongly (see Figure S2, Supporting Information). The ca. +98 ppm $NICS(2)_{zz}$ values of triplet [6 and 8]imperilene have opposite signs from the −44.4 and −49.5 ppm $NICS(0)_{zz}$ of triplet [12 and 16]trannulenes, respectively. The quintet states of the [n = even]imperilenes correspond to two triplet $4ne$ trannulenes and display aromaticity. The optimized geometries of the quintet states of [4, 6, and 8] imperilenes have equal CC(per) bond lengths (Table 1) and negative $NICS_{zz}$ values (Table 2).

Charged Imperilenes. Fokin et al. showed that oxidation of antiaromatic $4ne$ trannulenes gave aromatic 2+ charged species.[8] Thus, the −17 and −14 ppm NICS(0) values of the $C_{12}H_{12}{}^{2+}$ and $C_{10}H_{10}$ trannulenes were quite similar. Although we computed both the 2+ and 4+ charged [4, 6, and 8]imperilenes (see Tables S1 and S2, Supporting Information), only the 4+ species correspond to the 2+ trannulenes and had acceptable wave functions. The expected aromaticity of the 4+ charged [4, 6, and 8]imperilenes (each trannulenic perimeter has a 2+ charge and $4n + 2$ π electrons) is documented by the equal CC(per) bond lengths (Table S1) and by their generally large negative $NICS_{zz}$ values along the central axes (Table 2). The +33.8 ppm $NICS(0)_{zz}$ value in the center of [4]imperilene(4+) is quite exceptional in showing contributions from the σ-framework of the planar cyclobutane (see Figure S2 Supporting Information).

Imperilenes are a new class of molecules with appealing geometries comprised of two trannulenes generally isolated electronically by attachment to an intervening planar cycloalkane ring. Their aromatic/antiaromatic properties mirror those of the constituent trannulenes. The aromaticity of the singlet [5, 7, and 9]imperilene ground states and of the 4+ charged [4, 6, and 8]imperilenes, both having $4n + 2$ π electron trannulene units, is confirmed by their high symmetry and diatropic $NICS_{zz}$ values along the central axes. The higher energy quintet electronic states of the [4, 6, and 8]imperilenes also are aromatic, as they correspond to triplet $4n$ π electron trannulenes. In contrast, neutral singlet [4, 6, and 8]imperilenes are antiaromatic.

Acknowledgment. This work was supported in Georgia by NSF Grant CHE-0716718.

Supporting Information Available. Full ref 13, $NICS_{zz}$ grids of the different states of imperilenes, geometries and $NICS_{zz}$ of charged imperilenes, the frontier molecular orbitals, and Cartesian coordinates of all the optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.