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Can Bridged 1,6-X-[10]Annulenes ($X = SiH_2$, $SiMe_2$, PH, and S) Exist?

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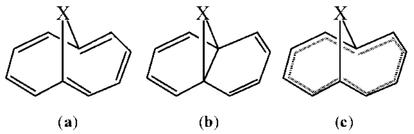
ABSTRACT

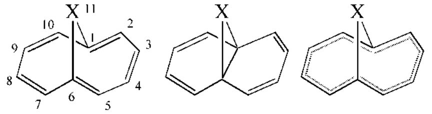


X = CH_2, O, NH, SiH_2, $SiMe_2$, PH, S

In contrast to the 1,6-X-[10]annulenes ($X = CH_2$, O, NH) with delocalized forms (c), their X = PH and S counterparts favor the bisnorcaradiene structures (b). Forms b and c are close in energy with $X = SiH_2$ and $SiMe_2$. The computed nucleus independent chemical shifts (NICS), show both annulenes (c) and cyclic polyenes (a) to be aromatic. Strain-introduced structural localization, e.g., due to four bulky $SiMe_3$ substituents, reduces but does not eliminate aromaticity.

The synthesis of 1,6-methano[10]annulene (**1**) in 1964 by Vogel[1] opened the area of bridged annulene chemistry. There are three possible types of structures for **1** and its derivatives: localized cyclic polyene **a** with alternating single and double bonds, bisnorcaradiene **b** with the strained three-membered ring, and the delocalized annulene **c** with strongly equalized C−C perimeter bond lengths.

The delocalized annulenic structure, **1c**, was established by a series of increasingly refined X-ray structures.[2] In addition, the ^1H NMR chemical shifts, in particular the upfield displacement of the hydrogens of the bridged methylene (−0.5 ppm) and the downfield shift of the olefinic protons (6.8−7.5 ppm), indicate the aromatic (cyclic delocalized) character of **1c**.[1]



a (C_s) **b** (C_{2v} or C_s) **c** (C_{2v} or C_s)

X = **1** (CH_2), **2** (O), **3** (NH), **4** (SiH_2), **5** ($SiMe_2$), **6** (PH), **7** (S)

However, some substituents (e.g., $X = C(CN)_2$) attached to the bridge carbon center can shift the valence tautomeric equilibrium to the **1b** side.[3] Bulky substituents (e.g., 2,5,7,-10-tetrakis(trimethylsilyl)) attached to the olefinic carbons

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favor the localized polyene **1a**-$(Me_3Si)_4$, as indicated (X-ray) by the strongly alternating bond lengths (1.45−1.47 vs 1.35−1.36 Å).[4] On this basis, it was concluded that the aromaticity is eliminated as a result of the strain effects. We challenge this conclusion here.

1,6-Oxido[10]annulene **2** (X = O) was synthesized independently by Vogel[5] and by Sondheimer[6] in 1964. The 1,6-imino[10]annulene **3** (X = NH) was reported 1 year later by Vogel.[7] Both **2** and **3** are aromatic and have ^{1}H NMR chemical shifts similar to that of **1**.

Theoretically, **1** and **2** have generally been computed at low ab initio levels (small basis sets and without electron correlation)[8] and with semiempirical methods.[9] However, electron correlation is very important for delocalized systems and influences the geometries and the energies.[10] Recent computations are based only on the semiempirical (AM1) and low level ab initio HF (3-21G and 6-31G*) methods.[11] Thus, a reexamination of these systems with electron correlation using adequately large basis sets is necessary. In addition, the corresponding silano (**4**, **5**), phosphino (**6**), and sulfido (**7**) systems are still unknown experimentally and have not yet been examined theoretically. What are the more favorable structures of **4**−**7**? Do they resemble **1**−**3** both geometrically and energetically?

We now present adequately high-level theoretical results to stimulate experimental investigations of the unknown derivatives. Geometry optimizations and frequency analyses were carried out with density functional theory (DFT) using the B3LYP method and the 6-311+G** basis set, as in the Gaussian 98 program.[12]

Structure and Energies. At the uncorrelated HF/6-31G* level, the localized **1a** (C_s) and **1b** (C_{2v}) are energy minima, and the delocalized **1c** (C_{2v}) is the transition state for the valence isomerization of **1a**. All three HF/6-31G* structures are nearly isoenergetic (Table 1): **1a** (0.0) > **1b** (0.2) > **1c** (0.5). However, these HF/6-31G* results do not agree with the experimental findings that only the delocalized **1c** is a stable molecule.[1]

Table 1. Relative Energies (kcal/mol) of **1**−**7**

X	a	b	c
CH_2 (**1**)^a	0.0^a	0.2^a	0.5^a
	(4.1)^b	(15.8)^b	0.0
O (**2**)	(5.3)^b	(16.0)^b	0.0
NH (**3**)	(4.7)^b	(16.7)^b	0.0
SiH_2 (**4**)	(7.3)^b	3.4	0.0
$SiMe_2$ (**5**)	(7.8)^b	2.1	0.0
PH (**6**)	(14.6)^b	0.0	7.7
S (**7**)	(18.1)^b	0.0	10.9
1-$(Me_3Si)_4$	0.0^c		3.1^c

^{a} HF/6-31G* energies. ^{b} B3LYP/6-311+G** single-point energies (in parentheses) with the HF/6-31G* geometries, since these species do not exist at B3LYP/6-311+G**. ^{c} Minima at B3LYP/6-31G*.

At B3LYP/6-311+G**, both **1a** and **1b** disappear and collapse upon optimization into the delocalized **1c**. Frequency analysis indicates that **1c** is the true energy minimum, in agreement with the experiment. The structural parameters agree with the X-ray data. The calculated C_1-C_6 separation, 2.279 Å, is close to the X-ray value (2.235 Å); the bond length alternations, defined as the difference between the longest and shortest bonds, are 0.033 and 0.046 Å, respectively. B3LYP/6-311+G** single-point calculations with the HF/6-31G* geometries of **1a** and **1b** give energies 4.1 and 15.8 kcal/mol higher than that of **1c** (Table 1). Thus, the HF results are not reliable, and we only discuss our B3LYP/6-311+G** data for the other systems (**2**−**7**).

At B3LYP/6-311+G**, only the delocalized 1,6-oxido (**2c**) and 1,6-imino (**3c**) systems are minima, in agreement with experimental findings. The C_1-C_6 separations, 2.209 (**2c**) and 2.237 Å (**3c**), as well as the bond length alternations, 0.021 (**2c**) and 0.028 Å (**3c**), are close to the **1c** values (2.279 and 0.033 Å). These data indicate delocalized structures for **2** and **3**. However, do the 1,6-silano (**4, 5**), 1,6-phosphino (**6**), and 1,6-sulfido (**7**) analogues mimic **1**−**3**?

Both the delocalized annulenic **4c** and the bisnorcaradienic **4b** are minima at B3LYP/6-311+G**; the former is 3.4 kcal/mol more stable than the latter. At 298 K, the calculated free energy difference ($\Delta G°$)[13] is −2.9 kcal/mol. Therefore, there is hardly any equilibrium concentration of **4b** on the basis of $\Delta G° = -RT \ln K$, and **4c** is the only detectable isomer. Furthermore, we have computed the 11,11-dimethylsilano derivative (**5**). Like **4b** and **4c**, both **5b** and **5c** are minima, and **5c** is more stable than **5b** by 2.1 kcal/mol. However, the calculated free energy of $\Delta G° = -3.6$ kcal/mol at 298 K reveals **5c** to be the only significantly populated isomer. In comparison with **1**−**3**, silano bridging (SiH_2 and $SiMe_2$) reduces the energy difference between **4b**/**5b** and **4c**/**5c** considerably.

At B3LYP/6-311+G**, the C_1-C_6 separations are 1.622 (**4b**) and 2.513 Å (**4c**), as well as 1.652 (**5b**) and 2.450 Å (**5c**), the corresponding bond length alternations are 0.043

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(13) The thermal energies (E_{th}) at 298 K are 107.3 (**4b**) and 107.2 (**4c**), 144.5 (**5b**) and 145.4 (**5c**) kcal/mol; the entropies are 92.3 (**4b**), 90.4 (**4c**), 103.2 (**5b**), and 108.4 (**5c**) cal/mol T.

Table 2. Strain of Three-Membered Rings; Bond Parameters of **1**−**7**

X	strain[a]	C_1−C_6[b]	WBI[c]	$C_1C_{11}C_6$[d]	CXC[e]
CH_2	26.8	2.279	0.007	99.6	113.0
NH	24.2	2.237	0.142	102.9	113.4
O	21.1	2.209	0.125	105.2	112.7
SiH_2	40.3	2.513	0.218	85.8	111.6
		1.622	0.930	50.8	
$SiMe_2$	41.2	2.450	0.271	82.5	109.5
		1.662	0.906	52.4	
PH	20.4	1.529	0.995	46.0	100.4
S	16.1	1.506	1.011	45.9	99.7

[a] In kcal/mol, based on eq 1; see ref 14. [b] The **1**−**7** C_1−C_6 separation. [c] The Wiberg bond index for C_1−C_6 in **1**−**7**. [d] The $C_1C_{11}C_6$ bridge angle in **1**−**7**. [e] The central angle in H_3CXCH_3.

(**4c**) and 0.048 Å (**5c**). Note that the C_1−C_6 separations in **4b** (1.622 Å) and **5b** (1.662 Å) are longer than in silacyclopropane (1.553 Å) at the same level of theory.

The phosphino (**6**) analogues mimic the silano (**4**, **5**) systems qualitatively. At B3LYP/6-311+G**, both the bisnorcaradienic **6b** and the annulenic **6c** are minima. However, the former is 7.7 kcal/mol lower in energy than the latter. This is in sharp contrast to **1b**−**3b**, which are 15.8−16.7 kcal/mol higher in energy than **1c**−**3c**. The barrier from **6c** to **6b** is computed to be only 1.5 kcal/mol at B3LYP/6-311+G** + ZPE (B3LYP/6-311+G**). Hence, **6b** should be the only observable phosphino isomer. Similar results are found for the sulfido systems (**7**). For example, both **7b** and **7c** are minima at B3LYP/6-311+G**, but the norcaradienic structure (**7b**) is 10.9 kcal/mol lower in energy than the delocalized form (**7c**). Since the isomerization barrier from **7c** to **7b** is only 1.8 kcal/mol [B3LYP/6-311+G** + ZPE (B3LYP/6-311+G**)], **7b** should be the only observable form.

The relative energies of the **1**−**7** forms in Table 1 depend, in part, on strain factors and are consistent with the known variations in strain of three-membered heterocycles (*c*-XC_2H_4).[14] These strain energies have been reevaluated in Table 2 at the same DFT level using acylic reference molecules:

$$H_3CXCH_3 + 2C_3H_8 = c\text{-}XC_2H_4 + 3C_2H_6 \qquad (1)$$

The large strain energies decrease modestly for the first row substituents, from X = CH_2 to NH and O, **1**−**3**. While the strain energies are smaller for X = PH, S (due to the ca. 90° bond angle preference) than for X = NH, O, the opposite is true for X = SiH_2, $SiMe_2$ versus CH_2.[14] The reduced strain with X = PH and S results in more effective C_1−C_6 interaction and leads to the preference of the bisnorcaradiene forms (**b**). As indicated by the calculated Wiberg bond indexes in Table 2, **4c** and **5c** have the strongest C_1−C_6 homoconjugative interactions, despite their longer C_1−C_6 distances. Therefore, the compensation between C_1−C_6 stabilization and strain destabilization leads to the geometric and energetic changes for **4b/c** and **5b/c**.

Aromaticity. The aromaticity of the delocalized annulenic systems is documented clearly by the highly equalized bond lengths and particularly by the very distinctive ^{1}H chemical shifts. However, can the "localized" cyclic polyenes also be aromatic?

Since the evaluation of the aromatic stabilization energies (ASE) is problematical,[15] the geometrical parameters are used here to judge the degree of cyclic electron delocalization.[16] Since none of the polyene structures (**1a**−**7a**) are minima on the DFT potential energy surface, we give the HF/6-31G* optimized parameters in Table 3. The aromatic **1c**−**7c** have equalized C−C bond lengths (0.021−0.046 Å); this range is smaller than that of naphthalene at the same HF level (0.059 Å).

Table 3. GIAO-HF/6-31G* NICS Values (ppm) for **1**−**7**

	Δ_R[a] (Å)	NICS[6][b]	NICS[6′][b]	NICS[10][c]
1a	0.115	−16.4	−10.0	−24.3
1b	0.137	−4.5	−4.5	
1c	0.033	−17.7	−17.7	−29.8
2a	0.112	−13.0	−8.8	−21.0
2b	0.134	−3.8	−3.8	
2c	0.021	−17.1	−17.1	−28.1
3a	0.117	−14.9	−10.0	−24.0
3b	0.137	−4.2	−4.7	
3c	0.028	−16.7	−17.7	−28.3
4a	0.151	−8.9	−2.8	−11.0
4b	0.144	1.0	1.0	
4c	0.043	−16.7	−16.7	−25.9
6a	0.140	−12.3	−4.4	−15.1
6b	0.141	−1.7	−1.8	
6c	0.046	−16.2	−18.7	−28.5
7a	0.137	−12.5	−5.6	−17.4
7b	0.134	−2.7	−2.7	
7c	0.035	−17.4	−17.4	−29.1
1a-$(Me_3Si)_4$	0.076	−12.4	−3.9	−19.0
1c-$(Me_3Si)_4$	0.036	−14.5	−14.5	−27.0

[a] Difference between the longest and shortest C−C bond lengths, at the HF/6-31G* level. [b] For the localized polyene systems (**a**), NICS[6] is located at the geometrical center of the cyclohexatriene subunit, and NICS[6′] for the cyclohexadiene moiety. For the norcaradiene systems (**b**), both NICS[6] and NICS[6′] are located at the centers of the two cyclohexadienes. For the delocalized annulene systems (**c**), NICS[6] and NICS[6′] are the values for the two equivalent formal six-membered rings. [c] NICS[10] is at the center of the 10-membered ring perimeter in all cases.

The nonaromatic structures (**1b**−**7b**) have alternating C−C bond lengths of 0.134−0.144 Å, not far from the value in 1,3-cyclohexadiene (0.125 Å). Since the 0.112−0.151 CC

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alternations of polyenes (**1a**−**7a**) are similar to those of **1b**−**7b**, **1a**−**7a** might also be nonaromatic geometrically. However, note that the energy differences between **1a**−**3a** and **1c**−**3c** are very small (Table 1). Hence, **1a**−**3a** must also be stabilized to a large extent.

Many details are revealed by magnetic property analysis of the bridged annulenes, based on the nucleus-independent chemical shifts (NICS).[17] The aromatic character of **1c**−**7c** are indicated by the negative NICS values at the centers of each formal six-membered rings as well as at the centers of the 10 C's comprising the perimeter ring (Table 3). The NICS values at the centers of the cyclohexadiene rings in **1b**−**7b** show their nonaromatic character clearly.

However, compared with **1c**−**7c,** the formal six- and ten-membered rings also have very pronounced NICS values. As a result of the larger number of double bonds (and perhaps to C_1-C_6 homoaromatic character), NICS of the formal cyclohexatriene units are not only more negative than those of the cyclohexadiene units but also more negative than the benzene value (−11.5, ring center) at the same level. This indicates that the structurally localized cyclic polyenes also are aromatic.[18]

This conclusion is supported by the results for 2,5,7,10-tetrakis(trimethylsiyl)-1,6-methano[10]annulene **1a**-($Me_3Si)_4$.[4] The localized polyene structure with strongly alternating bond lengths is favored since the considerable strain among the bulky groups is reduced.[4] The calculated bond length alternations (1.44−1.47 vs 1.38−1.39 Å) agree well with the experimental values (1.45−1.47 vs 1.35−1.36 Å). However, the highly delocalized **1c**-($Me_3Si)_4$ "bond switching" structure (C_2 symmetry) also is a minimum, comparable to **1c**−**3c**. The calculated energy difference is 3.1 kcal/mol at B3LYP/6-31G* where the CC bond range is only 1.404 to 1437 Å.

Even though reduced to some extent, the NICS values at the center of the cyclohexadiene (−3.9 ppm) and of the cyclohexatriene (−12.4 ppm) moieties as well as at the center of the 10-membered ring (−19.0 ppm) in **1a**-($Me_3Si)_4$ indicate substantial cyclic electron delocalization. Therefore, bond length alternation does not eliminate the aromaticity of such bridged [10]annulenes. As expected, the bond-length-equalized C_2 isomer (**1c**-($Me_3Si)_4$) is more aromatic, as indicated by the GIAO NICS values of −14.5 and −27.0 ppm; these are comparable to those of **1c**−**7c**.

For comparison, benzene was deformed artificially by fixing the bond lengths to 1.341 and 1.466 Å (as found in 1,3-cyclohexadiene). After partial optimization, this deformed structure is only 6.8 kcal/mol higher in energy than fully relaxed benzene, despite the 0.125 Å bond alternation (larger than in **1a**-($Me_3Si)_4$). Since the aromatic stabilization energy (ASE) of benzene, based on cyclohexadiene, is 33 kcal/mol,[15b,19] the ASE of the deformed benzene also is large, 26 kcal/mol. In addition, the NICS value of the deformed benzene is −10.7, very close to that (−11.5) of benzene itself, and the proton chemical shifts are the same. These data show that greater bond length alternation, e.g., due to the strain effects of substituents, reduces but does not eliminate the aromatic character of benzene[20] and of bridged annulenes.

In agreement with the experimental findings, density functional computations show that the 1,6-methano (**1c**), 1,6-oxido (**2c**), and 1,6-imino (**3c**) [10]annulenes have delocalized structures and are the only minima. However, their 1,6-phosphino (**6**) and 1,6-sulfido (**7**) analogues favor the bisnorcaradiene forms energetically by 7.7 and 10.9 kcal/mol over the annulenic structures. For X = SiH_2 (**4**) and $SiMe_2$ (**5**), **4b** and **4c**, as well as **5b** and **5c**, are energy minima and close in energy, and the delocalized **4c**/**5c** are more stable than **4b**/**5b**.

On the basis of the magnetic properties, not only the annulenic structures but also their structurally localized forms are aromatic. Introduced strain effects, e.g., in **1a-**($Me_3Si)_4$,[4] do not eliminate the aromaticity.

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Supporting Information Available: Energetic data and coordinates for **1**−**7** and systems with X = CF_2, SiF_2, PF, and CMe_2. This material is available free of charge via the Internet at http://pubs.acs.org.

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