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# Aromaticity in Silole Dianions: Structural, Energetic, and Magnetic Aspects

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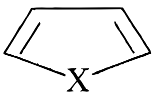
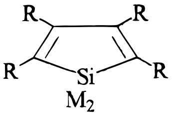
*Summary: Structural, energetic, and magnetic criteria confirm that the silole dianion $(CH)_4Si^{2-}$ (**7**) and its alkali-metal ion pairs, e.g. $(CH)_4SiLi^-$ (**7a**), $(CH)_4SiLi_2$ (**7b**), $(CH)_4SiNa_2$ (**13**), and $(CH)_4SiK_2$ (**14**), are highly aromatic. Inverse sandwich structures and strongly delocalized silole rings are prefered by **7b**, **13**, and **14**. The degree of aromaticity in $[\eta^5\text{-}(CH)_4Si]Li^-$ (**7a**) exceeds that of the isoelectronic third-period heterocycles $(CH)_4PLi$ (**5a**) and $(CH)_4SLi^+$ (**6a**) and even approaches that of $(CH)_5Li$ (**3a**).*

The lower aromaticity of the silolyl anion $(CH)_4SiH^-$ (**1**; $C_s$) and phosphole $(CH)_4PH$ (**2**; $C_s$), relative to their second-period congeners, the cyclopentadienyl anion $(CH)_5^-$ (**3**; $D_{5h}$) and pyrrole $(CH)_4NH$ (**4**; $C_{2v}$) (Table 1),[1] is due to the pyramidal ground-state geometries around the heteroatoms which result in poor conjugation. Inversion barriers involving these trivalent third-row elements[2] are quite high (Table 2). In both **1**[3] and **2**,[4] the aromaticity is greater in the planar $C_{2v}$ structures (which are the transition states). The overlap of 2p and 3p orbitals is *not* inherently poor.[2] Hence, reduction or elimination of the pyramidality problem should result in increased overlap and better conjugation in the third-period heterocycles. Indeed, the decreased pyramidality at silicon in lithium silolide, $(CH)_4SiHLi$ (**1a**), results in enhanced aromaticity relative to the free anion **1**.[3b]



| X= | | |
|---|---|---|
| SiH⁻ | **1** | ($C_s$) |
| SiHLi | **1a** | ($C_s$) |
| PH | **2** | ($C_s$) |
| CH⁻ | **3** | ($D_{5h}$) |
| CHLi | **3a** | ($C_{5v}$) |
| NH | **4** | ($C_{2v}$) |
| P⁻ | **5** | ($C_{2v}$) |
| PLi | **5a** | ($C_s$) |
| S | **6** | ($C_{2v}$) |
| SLi⁺ | **6a** | ($C_s$) |
| Si²⁻ | **7** | ($C_{2v}$) |
| SiLi⁻ | **7a** | ($C_s$) |



| M = | R = H | | R = Ph |
|---|---|---|---|
| Li | **7b** | ($C_{2v}$) | **8** |
| Na | **13** | ($C_{2v}$) | **9** |
| K | **14** | ($C_{2v}$) | **10** |
| Cl | **15** | ($C_{2v}$) | **11** |
| Me | | | **12** |

**Table 1. Aromatic Stabilization Energy ASE[a] (kcal mol⁻¹), Julg's Parameter *A*,[18] Bond Length Difference *D*[19] (Å), and Susceptibility Exaltation Λ[22] (10⁻⁶ cm³ mol⁻¹)**

| X | ASE | *A* | *D* | Λ |
|---|---|---|---|---|
| $SiH^{-\,b,c}$ (**1**; $C_s$) | 12.9 ($13.8^{d,e}$) | $0.971^f$<br>($0.926^{d,e}$) | $0.034^f$<br>($0.054^{d,e}$) | $-10.4^f$<br>($-7.7^{d,e}$) |
| $SiHLi^{c,g}$ (**1a**; $C_s$) | $32.0^{c,d}$ | 0.9996 | 0.004 | −14.1 |
| $PH^{d,e}$ (**2**; $C_s$) | 7.0 | 0.795 | 0.089 | −3.3 |
| $CH^{-\,d,e}$ (**3**; $D_{5h}$) | 28.8 | 1.0 | 0.0 | −17.2 |
| $CHLi^b$ (**3a**; $C_{5h}$) | 38.8 ($40.2^{c,d}$) | 1.0 | 0.0 | $-14.5^{c,g}$ |
| $NH^{d,e}$ (**4**; $C_{2v}$) | 25.5 | 0.967 | 0.037 | −12.1 |
| $P^{-\,d}$ (**5**; $C_{2v}$) | 29.0 | 0.997 | 0.011 | $-15.5^f$ |
| $PLi^b$ (**5a**; $C_s$) | 34.1 ($33.7^d$) | 0.998 | 0.007 | $-12.5^d$ |
| $S^{d,e}$ (**6**; $C_{2v}$) | 22.4 | 0.951 | 0.044 | −10.0 |
| $SLi^{+\,b}$ (**6a**; $C_s$) | 27.1 ($26.2^d$) | 0.961 | 0.039 | $-9.1^d$ |
| $Si^{2-\,f}$ (**7**; $C_{2v}$) | | 1.0 | −0.002 | −30.0 |
| $SiLi^{-\,b}$ (**7a**; $C_s$) | 36.4 ($40.4^d$) | 1.0 | −0.004 | $-20.7^d$ |
| $SiLi_2^f$ (**7b**; $C_{2v}$) | | 1.0 | −0.004 | −23.5 |
| $SiNa_2^d$ (**13**; $C_{2v}$) | | 0.999 | −0.006 | −18.2 |
| $SiK_2^{d,h}$ (**14**; $C_{2v}$) | | 0.999 | −0.006 | |
| $SiCl_2^b$ (**15**; $C_{2v}$) | −4.6 | 0.514<br>($0.153^i$) | 0.138<br>($0.184^i$) | $+6.2^f$ |

[a] For evaluation of the ASE (eq 1) the structures were optimized at the same levels as designed for the (hetero)cyclopentadiene and characterized as minima by RHF frequency calculations. Zero-point energies were scaled by 0.89.[27] The lithium ions are $\eta^1$, $\eta^3$, and $\eta^5$ coordinated in the (hetero)cyclopentane, (hetero)cyclopentene, and (hetero)cyclopentadiene systems, respectively. [b] RMP2(fc)/6-31+G* optimized. [c] Reference 3b. [d] RMP2(fc)/6-31G* optimized. [e] Reference 1a. [f] RMP2(fc)/6-31+G** optimized. [g] RMP2(fc)/6-31G** optimized. [h] For potassium, a (63311/53) SV basis set is used.[28] [i] Experimental average value of **11**.[16]

**Table 2. Inversion Barriers (kcal/mol) of Second- and Third-Row $AH_3$ Systems**

| | RMP2(fc)/6-31+G** + ZPE[a] | B3LYP/6-311+G** + ZPE[a] | exptl |
|---|---|---|---|
| $CH_3^-$ | 1.88 | 2.04 | |
| $SiH_3^-$ | 26.0 | 25.4 | 26.0 ± 6[b] |
| $NH_3$[c] | 4.1 | 3.1 | 5.2[d] |
| $PH_3$ | 33.9 | 32.9 | (31.5)[e] |

[a] Reference 27. [b] Reference 29. [c] The best theoretical barrier is 5.30 kcal/mol.[30] [d] Reference 30. [e] Reference 31.

The pyramidalization problem does not arise when divalent heteroatoms are involved, e.g. in the phospholyl anion $(CH)_4P^-$ (**5**; $C_{2v}$), in thiophene $(CH)_4S$ (**6**; $C_{2v}$), and in the isoelectronic silole dianion $(CH)_4Si^{2-}$ (**7**; $C_{2v}$). Derivatives of **5** (with divalent phosphorus) are known to have significantly greater aromatic character than those of **2** (with trivalent phosphorus ) (Table 1).[4,5] Similarly, five-[6] and six-membered[7] silacycles stabilized by adjacent nitrogen π-donor atoms are aromatic.

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(2) Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272.

(3) (a) Damewood, J. R., Jr. *J. Org. Chem.* **1986**, *51*, 5029. (b) Goldfuss, B.; Schleyer, P. v. R. *Organometallics* **1995**, *14*, 1553.

(4) Mathey, F. *Chem. Rev.* **1988**, *88*, 429 and references therein.

(5) More recently, the phospholyl anion was estimated to have 90.7% of the aromaticity of $(CH)_5^-$: Malar, E. J. P. *J. Org. Chem.* **1992**, *57*, 3694.

(6) Denk, M.; Lennon, R.; Hayashi, R.; West, R.; Belyakov, A. V.; Verne, H. P.; Haaland, A.; Wagner, M.; Metzler, N. *J. Am. Chem. Soc.* **1994**, *116*, 2691 and references therein.

(7) Nyulászi, L.; Kárpáti, T.; Veszprémi, T. *J. Am. Chem. Soc.* **1994**, *116*, 7239.

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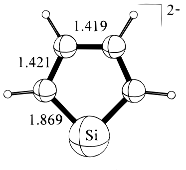


**Figure 1.** Silole dianion **7** (RMP2(fc)/6-31+G**; bond distances in Å; $C_{2v}$).

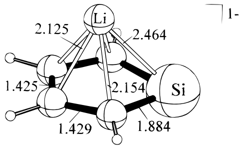


**Figure 2.** Lithium silole anion **7a** (RMP2(fc)/6-31+G*; bond distances in Å; $C_s$).

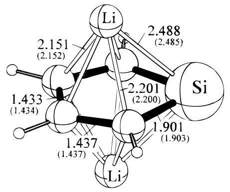


**Figure 3.** Dilithium silole **7b** (RMP2(fc)/6-31+G** (RMP2-(fc)/6-31G*); bond distances in Å; $C_{2v}$).

Alkali-metal triple ions of the 2,3,4,5-tetraphenylsilole dianion (**8**,[8,9] **9**,[10] **10**[11]) have been prepared. In **8**, the upfield $\delta(^{13}C_{\alpha/\beta})$ and the strongly downfield $\delta(^{29}Si)$ NMR signals (relative to those in 1,1,-dichloro-2,3,4,5-tetraphenylsilole (**11**)) are attributed to delocalization of negative charge associated with aromaticity. In recent developments, West et al. report an X-ray structure of **8**·5THF with $\eta^1/\eta^5$ coordination of the lithium ions.[12] Tilley's group finds a $\eta^5/\eta^5$ "inverse sandwich" coordination in the X-ray structure of a silole dianion with potassium counterions.[13]

We now report an *ab initio* study (using the GAUSSIAN 94[14] and IGLO[15] programs) of **7** (Figure 1), $(CH)_4SiLi^-$ (**7a**; $C_s$) (Figure 2), and its alkali-metal triple ions $(CH)_4SiLi_2$ (**7b**; $C_{2v}$) (Figure 3), $(CH)_4SiNa_2$ (**13**; $C_{2v}$) (Figure 4), and $(CH)_4SiK_2$ (**14**; $C_{2v}$) (Figure 5), as well as 1,1-dichlorosilole $(CH)_4SiCl_2$ (**15**; $C_{2v}$). These are model systems for **8**−**11** (an X-ray structure is reported for **11** in Figure 6).[16] Our data allow the aromatic character of these systems to be assessed on the basis of structural, energetic, and magnetic criteria. Our earlier examination of a diverse set of five-membered heterocycles showed how these three criteria could be directly and quantitatively correlated.[1a,c]

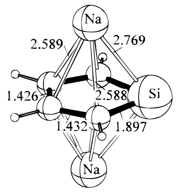


**Figure 4.** Disodium silole **13** (RMP2(fc)/6-31G*; bond distances in Å; $C_{2v}$).

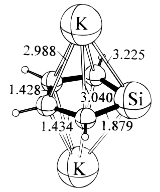
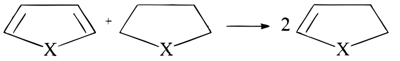


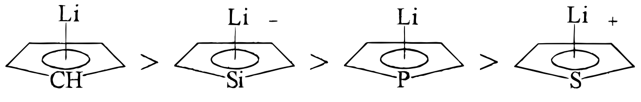
**Figure 5.** Dipotassium silole **14** (RMP2(fc); for Si, C, and H 6-31G* Gaussian standard basis set, for K, (63311/53) SV basis set;[28] bond distances in Å; $C_{2v}$).

The inverse sandwich structures **7b**, **13**, and **14**, with two $\eta^5$-coordinated alkali-metal ions, are consistent with delocalized negative charge, as expected for aromatic systems.[17] The equalized C−C bond lengths (Julg's parameter *A*,[18] Table 1) in **7**, **7a**, **7b**, **13**, and **14** indicate strong delocalization. All five structures exhibit even *inverted* butadiene distances: the bond length difference *D*[19] is slightly *negative* (Table 1).[20] The large p character on silicon in the Si−$C_\alpha$ $\sigma$-bonds may be responsible for the long Si−$C_\alpha$ distances in the delocalized triple ions **7b** (1.903 Å) and **13** (1.897 Å) (Table 3).[21] The structures of **11**[16] (1.832 Å, Figure 6) and **15** (1.857 Å) exhibit shorter Si−$C_\alpha$ bond lengths.

The aromatic stabilization energies (ASE; eq 1, Table 1) follow the **3a** > **7a** > **5a** > **6a** order. The silole



**(1)**



**3a** **7a** **5a** **6a**

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[8] Hong, J.-H.; Boudjouk, P.; Castellino, S. *Organometallics* **1994**, *13*, 3387.

[9] Goldfuss, B. Diplomarbeit, Erlangen, Germany, 1993.

[10] Joo, W.-C.; Hong, J.-H.; Chio, S.-B.; Son, H.-E. *J. Organomet. Chem.* **1990**, *391*, 27.

[11] Joo, W. C.; Park, Y. C.; Kang, S. K.; Hong, J.-H. *Bull. Korean Chem. Soc.* **1987**, *4*, 270.

[12] In the gas phase, however, the $\eta^5/\eta^5$ lithium coordination of **7b** is more stable: West, R.; Sohn, H.; Bankwitz, U.; Calabrese, J.; Apeloig, Y.; Mueller, T. *J. Am. Chem. Soc.* **1995**, *117*, 11608. For an X-ray structure of **12**, see: Párkányi, L. *J. Organomet. Chem.* **1981**, *216*, 9.

[13] Tilley, T. D.; et al. Personal communication (to be submitted for publication).

[14] Gaussian 94, Revision B.2: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Rahavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A., Gaussian, Inc., Pittsburgh, PA, 1995.

[15] Kutzelnigg, W.; Schindler, M.; Fleischer, U. *NMR Basic Princ. Prog.* **1990**, *23*, 165.

[16] Crystal data for **11**: $M_r = 455{,}43$; tetragonal; space group $I4_1/a$; $a = b = 26.626$ Å, $c = 13.330$ Å; $V = 9450(3)$ Å$^3$; $D_{calc} = 1.280$ Mg m$^{-3}$; $Z = 16$; $F(000) = 3776$; Mo K$\alpha$ ($\lambda = 0.710\ 73$ Å); $T = 298(2)$ K; data were collected with a Siemens P4 diffractometer on a crystal with the dimensions 0.4 × 0.4 × 0.3 mm using the $\omega$-scan method (3.0° < $2\Theta$ < 54.0°). Of a total of 4052 collected reflections 6742 were unique and 1413 with $I > 2\sigma(I)$ were observed. The structure was solved by direct methods using SHELXTL Plus 4.11. A total of 280 parameters were refined, with all data by full-matrix least squares on $F^2$ using SHELXL93 (G. M. Sheldrick, Göttingen, Germany, 1993). All non-hydrogen atoms were refined anisotropically; the hydrogen atoms were fixed in idealized positions using a riding model. Final *R* values: R1 = 0.0807 ($I > 2\sigma(I)$) and wR2 = 0.3049 (all data) with $R1 = \sum|F_o - F_c|/\sum F_o$ and $wR2 = \sum w|(F_o^2 - F_c^2)^2|/\sum(w(F_o^2)^2)^{0.5}$; largest peak 0.210 e Å$^{-3}$ and hole −0.241 e Å$^{-3}$. Further details are available on request from the Director of the Cambridge Crystallographic Data Center, Lensfield Road, GB-Cambridge CB2 1EW, U.K., by quoting the journal citation.

[17] Such $\eta^5$ counterion coordination of aromatic siloles has precedents in **1a**[3b] and in the $\{Cp^*Ru(H)[\eta^5\text{-}Me_4C_4SiSi(SiMe_3)_3]\}[BPh_4]$ complex: Freeman, W. P.; Tilley, T. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1994**, *116*, 8428.

[18] Julg's parameter (*A*) defines the degree of aromaticity in terms of deviations of (*n*) individual C−C bond lengths ($r_i$) from the mean carbon bond length (*r*): $A = 1$ for benzene ($D_{6h}$) and $A = 0$ for Kekulé benzene ($D_{3h}$), assuming C−C distances of 1.33 and 1.52 Å. $A = 1 - (225/n)\sum(1 - r_i/r)^2$: (a) Julg, A.; Francois, P. *Theor. Chim. Acta* **1967**, *7*, 249. (b) Kerk, S. M. v. d. *J. Organomet. Chem.* **1981**, *215*, 315.

[19] $D = C_\beta C_\beta - C_\alpha C_\beta$.

[20] Inverted C−C distances also are calculated in the $C_{2v}$ transition structure of the silolyl anion **1**.[3b]

[21] Bent, H. A. *Chem. Rev.* **1961**, *61*, 275.

**Table 3. Bond Lengths (Å), Wiberg Bond Indices (WBI), and Silicon Hybridizations in the Si−$C_\alpha$ $\sigma$-Bonds**[a]

| | **7** ($C_{2v}$)[b] | **7b** ($C_{2v}$)[c] | **13** ($C_{2v}$)[c] | **15** ($C_{2v}$)[c] |
|---|---|---|---|---|
| Si−$C_\alpha$, WBI | 1.869, 1.103 ($sp^{3.75}$) | 1.903, 1.054 ($sp^{6.27}$) | 1.897, 1.065 ($sp^{5.95}$) | 1.857, 0.735 ($sp^{2.52}$) |
| $C_\alpha$−$C_\beta$, WBI | 1.421, 1.457 | 1.437, 1.383 | 1.432, 1.418 | 1.354, 1.914 |
| $C_\beta$−$C_\beta$, WBI | 1.419, 1.356 | 1.434, 1.383 | 1.426, 1.375 | 1.492, 1.049 |

[a] "Natural population analysis" of the SCF density.[25] [b] RMP2(fc)/6-31+G** optimized. [c] RMP2(fc)/6-31G* optimized.

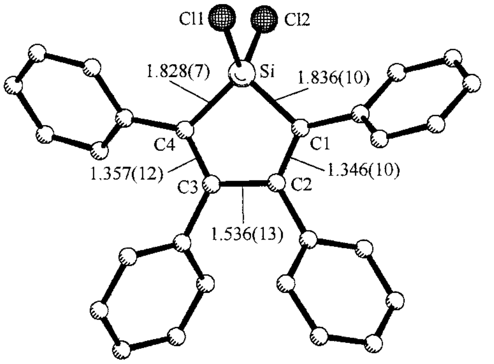

**Figure 6.** X-ray structure of 1,1-dichloro-2,3,4,5-tetraphenylsilole (**11**) (bond distances in Å; hydrogen atoms are omitted).[16]

**Table 4. IGLO Calculated**[a] **and Experimental Chemical Shifts *δ* and NPA Charges *q***[b]

| | $\delta(^{29}Si)$ | $q$(Si) | $\delta(^{13}C_\alpha)$ | $q(C_\alpha)$ | $\delta(^{13}C_\beta)$ | $q(C_\beta)$ |
|---|---|---|---|---|---|---|
| **7** | +51.88 | −0.040 | +145.13 | −0.904 | +119.18 | −0.425 |
| **7b** | +77.73 | +0.291 | +153.27 | −1.048 | +125.76 | −0.507 |
| **8**[c] | +68.54 | | +151.22[d] | | +129.71[d] | |
| **13** | +79.83 | +0.145 | +159.93 | −0.975 | +127.94 | −0.463 |
| **9**[e] | | | +153.74[d] | | +130.92[d] | |
| **15** | +14.95 | +1.754 | +135.54 | −0.758 | +160.74 | −0.189 |
| **11**[c] | +6.80 | | +132.28 | | +154.74 | |

[a] The IGLO (basis II)[15] chemical shifts are relative to the absolute shielding constants ($\sigma$) of TMS ($T_d$, //RMP2(fc)/6-31+G**): $\sigma$(Si) = 379.4, $\sigma$(C) = 197.5. [b] The SCF density was used.[25] [c] Experimental values.[8] [d] The $^{13}C_\alpha$/$^{13}C_\beta$ signals were interchanged. [e] Experimental values.[10]

$(CH)_4SiLi^-$ (**7a**; $C_s$) is not only more stabilized than the isoelectronic systems $(CH)_4PLi$ (**5a**; $C_s$) and $(CH)_4SLi^+$ (**6a**; $C_s$) but even approaches the ASE of $(CH)_5Li$ (**3a**; $C_{5v}$). The sequences for other aromaticity indices, Julg's parameters $A$,[18] the bond length differences $D$,[19] and the diamagnetic susceptibility exaltations $\Lambda$,[22] are similar (Table 1).

The diamagnetic susceptibility exaltations $\Lambda$[22] evaluated for **7**, **7a**, **7b**, and **13** are extraordinarily negative and point to large aromatic ring currents.[23] These are also responsible for the strongly shielded $Li^+$ ion ($\delta$-($^7$Li) −7.7 ppm)[24] in **7b**. In contrast, 1,1-dichlorosilole **15** exhibits a positive $\Lambda$ (+6.2, Table 1). This points to antiaromaticity in **15**, which is indeed supported by the negative ASE of **15** (−4.6 kcal/mol) and the localized C−C bond distances in **15** and in the X-ray structure of **11** (Table 1, Figure 5). Partial silylenium ion character results from the electron-withdrawing chlorine atoms.

In **8**, strong $\delta(^{29}Si)$ downfield and $\delta(^{13}C_{\alpha/\beta})$ upfield NMR displacements (relative to **11**) suggest "charge delocalization from silicon onto the ring".[8] In agreement with these experimental data, the calculated $\delta(^{29}Si)$ resonances for **7**, **7b**, and **13** are strong deshielding relative to **15** (Table 4). Natural population analysis,[25] however, does not show charge transfer from silicon to the ring carbons (Table 4). In **7**, **7b**, and **13**, the negative charges increase (relative to **15**) more on silicon than on the carbon atoms. The interpretive framework provided by the IGLO[15] program indicates that the $\delta(^{29}Si)$ deshielding in **7**, **7b**, and **13** is caused by paramagnetic contributions of the Si−$C_\alpha$ bonds and the "in plane" silicon lone pair. The strong deshielding of $\delta(^{31}P)$ in **5** relative to that in **2** is similar.[26] The strong paramagnetic contributions deshield $C_\alpha$ relative to $C_\beta$ in **7**, **7b**, and **13** (Table 4). This $\delta(^{13}C_\alpha) > \delta(^{13}C_\beta)$ signal order is also observed computationally for the isoelectronic $(CH)_4P^-$ (**5**) and experimentally for $(CH)_4PLi$ (**5a**).[26] Better agreement of $^{13}C_{\alpha/\beta}$ chemical shifts between **7b** and **8** as well as between **13** and **9** is apparent, if the published $C_\alpha$ and $C_\beta$ NMR signal assignments of **8**[8] and **9**[10] are interchanged (as in Table 4).

Hence, the high aromatic degree in the dianionic siloles **7**, **7a**, **7b**, **13**, and **14** is evident from structural, energetic, and magnetic aspects. These related criteria for aromaticity[1a,c] reveal that the dianionic siloles are more aromatic than isoelectronic phosphole and thiophene systems and even approach the aromaticity of the cyclopentadienyl anion.

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**Supporting Information Available:** Tables giving crystal data and structure refinement details, atomic coordinates, bond distances and angles, and thermal parameters for **11** (5 pages). Ordering information is given on any current masthead page.

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(22) $\Lambda$ is calculated (IGLO basis II[15]) as the difference between the magnetic susceptibility of the system ($\chi_M$) and the susceptibility estimated by an increment scheme for the hypothetical system without cyclic delocalization ($\chi_{M'}$): ($\Lambda = \chi_M - \chi_{M'}$). For applications of $\Lambda$ as criterion for aromaticity see refs 1a, 3b, 23, and: Dauben, H. J.; Wilson, J. D.; Laity, J. L. *J. Am. Chem. Soc.* **1969**, *91*, 1991.

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