mass spectrum (70 eV) of this material showed a 40.6:100 *m/e* 244:245 ratio. That for authentic Ph_3CD is 40.3:100. A Ph_3CD/Ph_3CH ratio of (96 ± 1):(4 ± 1) was calculated. The residue remaining after the hexanes extraction was taken up in $CHCl_3$. Ethylidene **10** was isolated by a procedure similar to the one given above. The H_α ^1H NMR resonance was absent, and the H_β ^1H NMR resonance (δ 2.52) was a singlet.

A septum-capped NMR tube was charged with **5**-α-d_2 (0.027 g, 0.044 mmol) and CD_2Cl_2 (0.350 mL). The tube was cooled to −78 °C, and $Ph_3C^+PF_6^-$ (0.019 g, 0.049 mmol) in CD_2Cl_2 (0.200 mL) was slowly added. After a thorough shaking, the tube was quickly transferred to a −73 °C NMR probe. A ^1H NMR spectrum showed the clean formation of **13**-d_2; no olefinic protons were detectable. The sample was warmed to room temperature, which allowed (as a result of slight chemical shift changes) the detection of Ph_3CH (δ 5.54). Solvent was removed from the reaction mixture, and the residue was applied to a silica gel preparative TLC plate. Elution with 1:4 ethyl acetate/hexanes gave a UV-active band with a R_f of ca. 0.7. Triphenylmethane (0.014 g, 0.036 mmol, 82%) was isolated from this band. Its 70-eV mass spectrum gave a 100:18.6 *m/e* 244:245 ratio, which was identical with that observed in commercial Ph_3CH.

A septum-capped NMR tube was charged with **2** (0.0101 g, 0.0176 mmol), **2**-α-d_2 (0.0104 g, 0.0180 mmol), and CH_2Cl_2 (0.300 mL). The tube was freeze–thaw degassed three times and cooled to −78 °C. Then 0.100 mL of a 0.071 M solution of $Ph_3C^+PF_6^-$ in CH_2Cl_2 (0.0071 mmol, 0.20 equiv) was added via gas-tight syringe. The reaction was kept at −78 °C for 0.5 h and then allowed to warm to room temperature over the course of 3 h. The content of the NMR tube were applied to a preparative TLC plate, and the triphenylmethane was isolated as described in the preceding paragraph. Analysis of the *m/e* 244:245 ratio in the 70-eV mass spectrum indicated a (84 ± 1):(16 ± 1) Ph_3CH/Ph_3CD ratio.

A septum-capped NMR tube was charged with (*SS,RR*)-**7** (0.0089 g, 0.0137 mmol), (*SS-RR*)-**7**-β-d_3 (0.0092 g, 0.0141 mmol), and CH_2Cl_2 (0.300 mL). The tube was freeze–thaw degassed three times and cooled to −78 °C. Then 0.100 mL of a 0.056 M solution of $Ph_3C^+PF_6^-$ in CH_2Cl_2 (0.0056 mmol, 0.20 equiv) was added via gas-tight syringe. The reaction was kept at −78 °C for 0.5 h and then allowed to warm to room temperature over the course of 3 h. The contents of the NMR tube were applied to a preparative TLC plate and the triphenylmethane was isolated as described above. Analysis of the *m/e* 244:245 ratio in the 70-eV mass spectrum indicated a (86 ± 1):(14 ± 1) Ph_3CH/Ph_3CD ratio.

Acknowledgment. This investigation was supported by the Department of Energy (regiochemistry) and the NIH (Grant GM 29026-01; stereochemistry). FT NMR and mass spectral measurements made use of spectrometers obtained via NSF Departmental instrumentation grants and the University of Utah Institution Funds Committee. W.A.K. thanks the Regents of the University of California for a Fellowship.

Registry No. 1, 71763-23-0; **2**, 74540-90-2; **2**-α-d_2, 74540-81-1; (*SR,RS*)-**2**-α-d_1, 85926-89-2; (*SS,RR*)-**2**-α-d_1, 85955-96-0; **3**, 74540-91-3; **4**, 85926-72-3; **5**, 85926-73-4; **5**-α-d_2, 85939-48-6; **6**, 85926-74-5; (*SS,RR*)-**7**, 82399-54-0; (*SR,RS*)-**7**, 82374-39-8; **8**, 85956-36-1; **9**, 85926-75-6; **10k**, 74540-80-0; **10**t, 74561-66-3; **10k**-α-d_1, 85955-98-2; **10t**-α-d_1, 85956-00-9; **10**-β-d_3, 85926-91-6; **11k**, 74540-85-5; **11**t, 74561-68-5; **12k**, 85926-77-8; **12**t, 85955-88-0; **13**, 85926-83-6; (*RR,SS*)-**14**, 85926-79-0; (*RS,SR*)-**14**, 85955-90-4; (*RR,SS*)-**15**, 85926-81-4; (*RS,SR*)-**15**, 85955-92-6; **16k**, 85926-85-8; **16**t, 85956-02-1; (*SS,RR*)-**17**, 85926-86-9; (*SR,RS*)-**17**, 85955-93-7; (*SS,RR*)-**18**, 85926-88-1; (*SR,RS*)-**18**, 85955-95-9; (η-C_5H_5)Re(NO)(PPh_3)(CH_3), 71763-18-3; (η-C_5H_5)Re(NO)(PPh_3)($COCH_2C_6H_5$), 82582-48-7; (η-C_5H_5)Re(NO)(PPh_3)(CO_2CH_3), 82293-79-6; $Ph_3C^+PF_6^-$, 437-17-2; $Li(C_2H_5)_3BD$, 74540-86-6; $C_6H_5CH_2Br$, 100-39-0; C_6H_5Br, 108-86-1; PMe_3, 594-09-2.

Are the Silacyclopentadienyl Anion and the Silacyclopropenyl Cation Aromatic?

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Abstract: Stabilization energies attributable to aromaticity in the silacyclopentadienyl anion and the silacyclopropenyl cation were found to be small in the former and absent in the latter when calculated from bond-separation reactions employing 3-21G and STO-2G basis sets. The silacyclopentadienyl anion is approximately 25% as aromatic as the all-carbon analogue whereas silabenzene is more than 80% as aromatic as benzene. The introduction of diffuse functions into the basis sets has only a small effect on these results. The silacyclopropenyl cation is actually destabilized but strain is probably a key factor in the comparison. Also found was that the STO-2G basis set gives geometries and relative energies consistent with those of a larger basis set and that the semiempirical INDO method may be useful for predicting the structures of larger systems for which geometry optimizations even with STO-2G may be too time consuming.

The long-standing interest on the part of chemists in isolating and characterizing unsaturated silicon has dramatically increased in intensity in the past 10 years.[1] With the exception of a few papers,[2] however, relatively little attention has been paid to the subject of aromatic silicon. From a computational point of view, part of the reason for this is that the size of aromatic systems prevents extensive ab initio calculations with large basis sets.

The present paper has two goals: to investigate the possibility of aromaticity in two simple silacyclo ions and to assess potentially time-saving approaches to larger systems. The $4n + 2$ π electron network in the cyclopentadienyl anion is isoelectronic with that in benzene, and the six π electrons are spread symmetrically among the five carbons in the ion. As a result, one might expect substantial delocalization stabilization in the latter. Silabenzene is apparently nearly as aromatic as benzene;[2b] thus, similar comments presumably apply to the silacyclopentadienyl anion. In the latter system, however, the symmetry is partially destroyed, so the negative charge need not be spread evenly throughout the mol-

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[1] L. E. Gusel'nikov and N. S. Nametkin, *Chem. Rev.*, **1979**, *79*, 531.

[2] (a) T. J. Barton and D. S. Banasiak, *J. Am. Chem. Soc.*, **1977**, *99*, 5199; T. J. Barton and G. T. Burns, *ibid.*, **1978**, *100*, 5199; H. Bock, A. Bowling, B. Solouki, T. J. Barton, and G. T. Burns, *ibid.*, **1980**, *102*, 429; C. L. Kreil, D. L. Chapman, G. T. Burns, and T. J. Barton, *ibid.*, **1980**, *102*, 841; G. Maier, G. Mihm, and H. P. Reisenhauer, *Angew. Chem.*, **1980**, *92*, 58 [*Angew. Chem., Int. Ed. Engl.*, **1980**, 19, 52]; B. Solouki, P. Rosmos, H. Bock, and G. Maier, *Angew. Chem.*, **1980**, *92*, 56 [*Angew. Chem., Int. Ed. Engl.*, **1980**, *19*, 51]; T. J. Barton and M. Vuper, *J. Am. Chem. Soc.*, **1981**, *103*, 6788. (b) H. B. Schlegel, B. Coleman, and M. Jones, *ibid.*, **1978**, *100*, 6499; P. H. Blustin, *J. Organomet. Chem.*, **1979**, *166*, 21.

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ecule. If this loss of symmetry results in a buildup in negative charge at silicon, one expects the system to be destabilized. The two π-electron three-membered rings are also potentially aromatic, according to the $4n + 2$ rule. Here, however, one has only two π electrons spread over three heavy atoms, and strain in the small rings will tend to destabilize them.

Previous calculations on silabenzene[2b] have been carried out with the minimal basis set STO-3G[3] method. As the number of atoms in the molecule increases, the size of the Gaussian expansion in the minimal basis set becomes important with regard to computer time. It has been pointed out[4] that the smaller STO-2G[3] expansion often does an acceptable job in predicting geometries, and this method is tested further in the present paper. The potential ability of the semiempirical INDO[5] method to predict geometries of large silicon-containing systems is probed as well.

Computational Approach

Unless otherwise noted, all geometries have been fully optimized with the STO-2G basis set, using the optimization methods in HONDO[6] and GAUSS80.[7] The STO-2G valence scale factor for Si is taken from the work of Gordon and Marsh.[10] The cyclic anions and cations have been assumed to be planar. Energy comparisons are made at both the STO-2G and split-valence 3-21G[8] levels. Because diffuse orbitals may be important in the description of anions, an additional set of calculations have been performed in which such functions are incorporated into both basis sets. For one molecule, silabenzene, the geometry has also been optimized with INDO using the method developed by McIver and Komornicki.[9]

Results and Discussion

A. Molecular Orbitals. Schematics of the π molecular orbitals for all of the systems being considered here are presented in Figure 1. The orbitals of benzene (Figure 1a) are well known, and those of silabenzene are quite similar. Introduction of a silicon splits the benzene e_{1g} pair into b_1 and a_2, with the a_2 MO lying slightly lower in energy because of its node through Si. The highest lying b_1 orbital is polarized toward the Si and the para carbon, while the lower lying b_1 MO is strongly polarized away from silicon.

Except for the fact that there is one less carbon, the orbitals of the cyclopentadienyl anion and its silicon analogue (Figure 1b) are much the same as those in Figure 1a. The MO coefficients in b_1 and a_2 (E_1'' in the hydrocarbon) are very similar in the two ions. In the b_1 component, the contribution from the carbons adjacent to X is small, while a_2 is polarized toward these carbons. For X = Si, the a_2 MO is again slightly lower in energy. The orbital denoted b_1 in Figure 1b is symmetric in the hydrocarbon and polarized away from silicon in the silacyclopentadienyl anion. The π MO for the three-membered ring is depicted in Figure 1c. This orbital is symmetric in cyclopropenyl (a_2'') and slightly polarized toward the carbons in the silicon analogue (b_2).

B. Electron-Density Distributions. The electron densities in the ions relative to the neutral parent molecules are shown in Figure 2 for both basis sets. In the three-membered rings, the positive charge is spread more evenly among all atoms, although the larger basis set actually predicts a greater increase in positive charge on carbon than on silicon. This is somewhat misleading since, in the cation, the carbon is still slightly negative, whereas the silicon has a very large positive charge. In the five-membered rings, the silicon accepts a large increase in electron density, while carbon undergoes a much smaller change. This is likely to destabilize the silicon. For both species, the larger basis set predicts a greater increase in electron densities on the hydrogen than on the carbons to which they are attached.

Table I. STO-2G Prototype Geometries[a]

molecule	geometric parameters
CH_4	$R = 1.089\ (1.086)$
SiH_4	$R = 1.485\ (1.481)$
CH_3^+	$R = 1.128\ (1.079)$, $\alpha = 120.0\ (120.0)$
CH_3^-	$R = 1.118\ (1.121)$, $\alpha = 98.3\ (103.1)$
SiH_3^+	$R = 1.515\ (1.463)$, $\alpha = 120.0\ (120.0)$
SiH_3^-	$R = 1.501\ (1.562)$, $\alpha = 93.4\ (95.2)$
$H_2C{=}CH_2$	$R(CC) = 1.318\ (1.33)$, $\alpha(HCC) = 122.3\ (121.7)$, $R(CH) = 1.089\ (1.076)$
$H_3C{-}CH_3$	$R(CC) = 1.538\ (1.526)$, $R(CH) = 1.092\ (1.088)$, $\alpha(HCC) = 111.1\ (111.5)$
$H_2C{=}SiH_2$	$R(SiH) = 1.479\ (1.474)$, $R(CSi) = 1.707\ (1.718)$, $R(CH) = 1.088\ (1.074)$, $\alpha(HCSi) = 123.3\ (122.6)$, $\alpha(HSiC) = 121.2\ (122.2)$
$H_3C{-}SiH_3$	$R(CSi) = 1.929\ (1.867)$, $R(CH) = 1.089\ (1.093)$, $R(SiH) = 1.485\ (1.485)$, $\alpha(HCSi) = 110.9\ (111.2)$, $\alpha(HSiC) = 110.5\ (110.6)$
C_6H_6	$R(CC) = 1.398\ (1.397)$, $R(CH) = 1.090\ (1.084)$

[a] Bond lengths in angstroms, angles in degrees. The experimental values (3-21G for unstable species) are given in parentheses.

Table II. Silabenzene Geometry[a]

	FSGO[b]	STO-3G[c]	STO-2G	INDO
$R(SiC)$	1.819	1.722	1.787	1.782
$R(C_1C_2)$	1.409	1.381	1.394	1.375
$R(C_2C_3)$	1.420	1.395	1.406	1.391
$R(SiH)$	1.446	1.419	1.476	1.484
$R(C_1H)$	1.097	1.079	1.089	1.117
$R(C_2H)$	1.088	1.086	1.092	1.125
$R(C_3H)$	1.099	1.080	1.090	1.122
$\alpha(CSiC)$	102.7	110.3	107.6	107.4
$\alpha(CCSi)$	122.5	117.4	118.3	118.0
$\alpha(C_1C_2C_3)$	122.7	125.1	125.2	125.6
$\alpha(C_2C_3C_4)$	126.9	124.6	125.4	125.4
$\alpha(SiCH)$	123.0		123.9	126.3
$\alpha(HC_2C_1)$	120.4	118.4	118.2	117.7

[a] Angles in degrees, bond lengths in angstroms; the numbering system refers to Figure 3. [b] Reference 2b of text. [c] Reference 2b of text.

Table III. Geometries for Three-Membered Rings[a]

	neutral[b]		ion	
	X = C	X = Si	X = C	X = Si
$R(XC)$	1.523	1.869	1.394	1.772
$R(CC)$	1.282	1.324	1.391	1.393
$R(XH)$	1.074	1.480	1.105	1.501
$R(CH)$	1.060	1.067	1.105	1.101
$\alpha(CXC)$	49.8	41.5	60.0	46.3
$\alpha(HXC)$	119.2	121.7	150.0	156.9
$\alpha(HCC)$	149.4	136.4	150.0	136.8

[a] Bond length in angstroms, angles in degrees. See schematic in Figure 4. [b] Structures are from 3-21G, see ref 14 of text.

C. Geometries. To evaluate the ability of STO-2G to predict geometries, the structures predicted by this basis set are listed in Table I for a number of simple species that will be used in the energy comparisons in section D below. The structural parameters are compared with the experimental ones when they are known and with 3-21G values for ions and silaethylene. For the most part the agreement is excellent, although some of the ion bond lengths appear to be off by as much as 0.05 Å.

The predicted angles and bond lengths for silabenzene are listed in Table II for STO-2G, STO-3G,[2b] FSGO,[2b] and INDO, using the numbering system shown in Figure 3. The STO-3G and FSGO C-Si bond lengths bracket that predicted by STO-2G, and both former methods predict a much shorter Si–H bond length. For the latter STO-2G is in very good agreement with typical experimental values.[5] All methods predict a small C–Si–C angle, with STO-2G again being bracketed by the other two ab initio

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[3] W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **1969**, *51*, 2657.

[4] D. Poppinger, *Chem. Phys.*, **1976**, *12*, 131.

[5] M. S. Gordon, M. D. Bjorke, F. J. Marsh, and M. S. Korth, *J. Am. Chem. Soc.*, **1978**, *100*, 2670; J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **1967**, *47*, 2026.

[6] H. F. King and M. Dupuis, *J. Comput. Phys.* **1976**, *21*, 144; M. Dupuis and H. F. King, *Int. Quantum Chem.*, **1977**, *11*, 613; *J. Chem. Phys.*, **1978**, *68*, 3998.

[7] J. S. Binkley, R. A. Whiteside, R. Krishnan, R. Seeger, D. J. DeFrees, H. B. Schlegel, S. Topiol, L. R. Kahn, and J. A. Pople, *QCPE*, **1980**, *13*, 406.

[8] J. S. Binkley, J. A. Pople, and W. J. Hehre, *J. Am. Chem. Soc.*, **1980**, *102*, 939; M. S. Gordon, J. S. Binley, J. A. Pople, W. J. Pietro, and W. J. Hehre, *ibid.*, **1982**, *104*, 2797.

[9] J. W. McIver and A. Komornicki, *Chem. Phys. Lett.*, **1971**, *10*, 303.

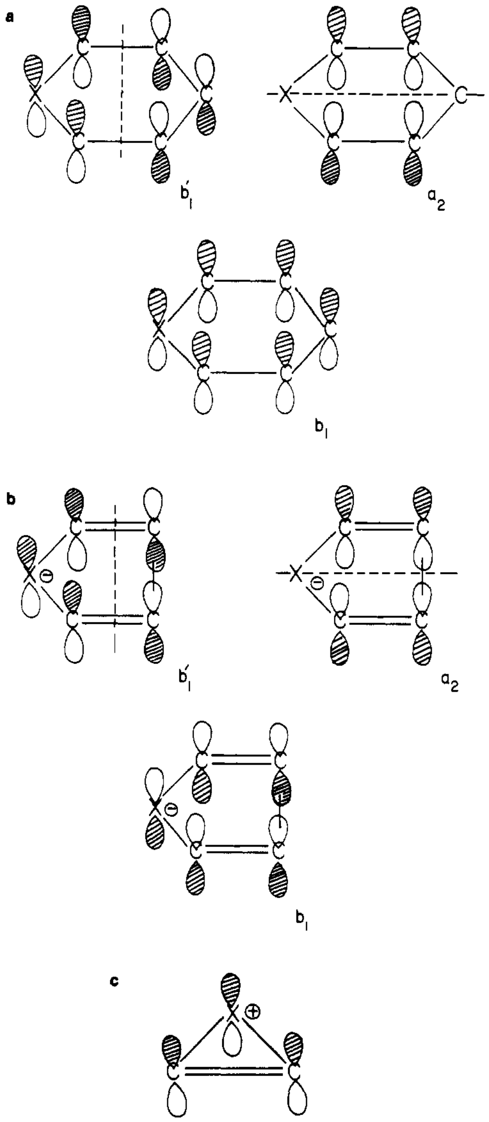

Figure 1. Schematics of occupied π MO's: (a) XC_5H_6; (b) $XC_4H_5^-$; (c) $XC_2H_3^+$.

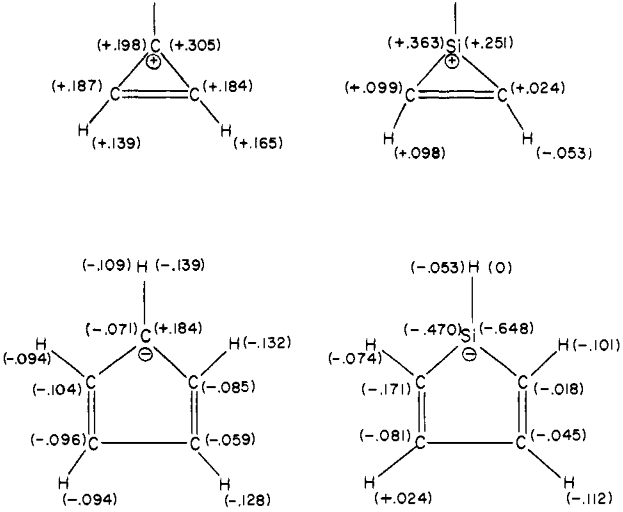

Figure 2. Change in electron densities. STO-2G values are given on the left and 3-21G on the right. A positive sign indicates an increase in positive charge.

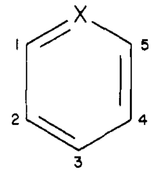

Figure 3.

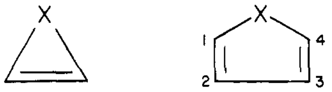

Figure 4.

Table IV. Geometries for Five-Membered Rings[a]

	neutral		ion	
	X = C	X = Si	X = C	X = Si
R(XC)	1.528	1.913	1.404	1.821
R(C_1C_2)	1.332	1.331	1.404	1.377
R(C_2C_3)	1.500	1.511	1.404	1.433
R(XH)	1.098	1.487	1.087	1.468
R(C_1H)	1.088	1.087	1.087	1.088
R(C_2H)	1.089	1.091	1.087	1.089
α(HXC)	112.0	114.2	126.0	133.5
α(HC_1C_2)	127.3	123.2	126.0	121.4
α(HC_2C_1)	127.8	123.8	126.0	122.8
α(CXC)	101.9	90.1	108.0	93.0
α(XCC)	109.9	108.3	108.0	107.5
α(CCC)	109.2	116.7	108.0	116.0

[a] Bond lengths in angstroms, angles in degrees. See Figure 4 for numbering system.

methods. The difference between STO-2G and STO-3G is at least partially due to the different valence-scale factors used by the two methods. The value used here was chosen from STO calculations on diatomics[10] and has been used with some success in predicting geometries in organosilicon compounds.[11] The average of the STO-2G Si–C bond lengths in silaethylene and methylsilane is 0.03 Å longer than that found for silabenzene, so some stabilization due to delocalization is clearly indicated. Finally, note that the geometry predicted for silabenzene by INDO is in excellent agreement with the STO-2G structure. This is encouraging, particularly if one intends to study larger fused-ring systems.

A schematic and numbering system for the three-and five-membered rings is given in Figure 4, and the predicted geometries are listed in Tables III and IV. The cyclopropenyl cations have rather short XC bond lengths, considerably shorter than the average of isolated single and double bond lengths. With regard to stabilization of the rings, however, this is likely to be balanced by ring strain (see below).

The average of the STO-2G bond lengths for C_2H_6 and C_2H_4 is 1.428 Å. Comparison of this value with that predicted for cyclopentadienyl anion (Table IV) indicates substantial delocalization in the anion. Indeed, R(CC) in this anion is only slightly larger than that found for benzene (1.398 Å). In contrast, the calculated R(CSi) in the silacyclopentadienyl anion is slightly larger than the average of isolated single and double C–Si bond lengths and 0.035 Å longer than that in silabenzene. This is a preliminary indication that the stabilization due to delocalization in the silicon-containing anion is small.

D. Energetics. The foregoing discussion has been largely qualitative in nature, since no numerical value has been attached to the "aromaticity" or delocalization stabilization for any of the species considered here. One can, however, use the bond-separation reactions introduced by Pople and co-workers[12] to obtain a quantitative measure of aromaticity. The appropriate reactions and the calculated energy differences for the species of interest here are listed in Table V. Also listed in Table V is the ratio

$$R = \Delta E(X = Si)/\Delta E(X = C) \qquad (1)$$

where ΔE refers to the appropriate bond-separation reaction. It

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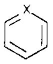
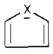
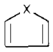
(10) F. J. Marsh and M. S. Gordon, *Chem. Phys. Lett.*, **1977**, *45*, 255.

(11) M. S. Gordon, *Chem. Phys. Lett.*, **1978**, *54*, 9.

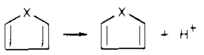
(12) W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Am. Chem. Soc.*, **1970**, *92*, 4796.

Table V. Bond-Separation Reactions[a]

reaction	ΔE(STO-2G)		ΔE(3-21G)		R[b]	
	X = C	S = Si	X = C	X = Si	STO-2G	3-21G
(A)  $+ 5CH_4 + XH_4 \rightarrow 2C_2H_6 + 2C_2H_4 + CH_3XH_3 + CH_2XH_2$	73	61	59	47	0.84	0.80
(B)  $+ XH_3^- + 4CH_4 \rightarrow C_2H_6 + 2C_2H_4 + 2CH_3XH_2^-$	102	25	87	23	0.24	0.26
(C)  $+ 4CH_4 + XH_4 \rightarrow C_2H_6 + 2C_2H_4 + 2CH_3XH_3$	14	9	10	4	0.64	0.40
(D)  $+ 2CH_4 + XH_3^+ \rightarrow C_2H_4 + 2CH_3XH_2^+$	−10	−30	−24	−57	3.00	2.37
(E)  $+ 2CH_4 + XH_4 \rightarrow C_2H_4 + 2CH_3XH_3$	−76	−62	−60	−46	0.82	0.77

[a] Energies in kcal/mol. [b] R = ratio of ΔE(X = Si)/ΔE(X = C).

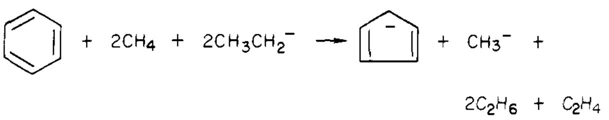
Table VI. Deprotonation Reactions[a]

reaction	ΔE							
	X = C				X = Si			
	STO-2G	3-21G	6-31G*	MP2/ 6-31G*	STO-2G	3-21G	6-31G*	MP2/ 6-31G*
$XH_4 \rightarrow XH_3^- + H^+$	24.6	20.1	19.8	19.9	19.4	16.5	16.9	16.7
$CH_3XH_3 \rightarrow CH_3XH_2^- + H^+$	24.4	20.0			20.1	17.1		
	20.3	16.5			20.1	17.0		

[a] Energies in eV.

is particularly important to note the generally good agreement between STO-2G and 3-21G for this ratio.

Both basis sets predict silabenzene to be about 80% as aromatic as benzene by this measure. Schlegel[2b] found a similar ratio with an analogous approach. A much larger difference between carbon and silicon is found for the cyclopentadienyl anions. The hydrocarbon anion is found to be more aromatic than benzene, while the delocalization stabilization in the silicon analogue is rather small.[13] The latter result is not unexpected in view of the predicted C–Si bond length and the large increase in negative charge on silicon. Qualitatively, one may relate the strong delocalization effect in cyclopentadienyl anion to the symmetric distribution of the negative charge throughout the molecule and to the sharing of six π electrons by only five carbons. An interesting quantitative probe of this may be obtained by taking the difference between reactions A and **B** in Table V, for X = °C:

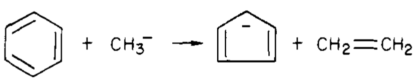


(2)

Reaction 2 measures the extra stabilization in the anion relative to benzene and has a ΔE of −28 (−29) kcal/mol for 3-21G (STO-2G). This reaction may in turn be viewed as a composite of reactions 3 and 4. Reaction 3 measures the relative deprotonation energies of methane and ethane and is nearly thermoneutral. Thus the relative delocalization stabilization of cyclopentadienyl anion and benzene is approximately represented by (4). The latter clearly depicts the extra stability of the anion due to the extra π electrons. Equation 4 also demonstrates that the delocalization of the negative charge in the cyclopentadienyl anion is energetically more effective than delocalization of the π electrons in benzene.

$$2CH_4 + 2CH_2CH_2^- \rightarrow 2CH_3^- + 2C_2H_6 \qquad (3)$$

ΔE(STO-2G) = 10 kcal/mol; ΔE(3-21G) = 6 kcal/mol



(4)

ΔE(STO-2G) = −39 kcal/mol; ΔE(3-21G) = −34 kcal/mol

Reaction 3 suggests an additional measure of "aromaticity" in the anions, namely, the energy of the deprotonation reactions

$$RH \rightarrow R^- + H^+ \qquad (5)$$

If R^- is unusually stable, one would expect ΔE for reaction 5 to be unusually small. The energies for a number of deprotonation reactions are listed in Table VI. For methane and silane, a polarization basis set (6-31G*[14]) and second-order perturbation theory (MP2[15]) are included to demonstrate that the predicted energy differences converge rapidly at the SCF level. Even though STO-2G tends to overestimate ΔE for deprotonation, the relative values are well reproduced. For the five-membered hydrocarbon ring the deprotonation energy drops by 4 eV relative to methane and ethane, indicative of the significant stabilizattion of the corresponding anion. In contrast, there is no change in the silicon ring relative to silane or methylsilane.

Returning to Table V, one finds that the bond-separation reactions for the cyclopropenyl cations are exothermic, indicating a destabilization. It must be recognized, however, that these rings are highly strained. Therefore, reaction D in Table V is measuring ring strain as well as the effect of delocalization. To approximately separate the two effects, consider the bond-separation reactions for the neutral rings (reaction E in Table V). Comparison of reactions D and E suggest that the cyclopropenyl cation is substantially stabilized by delocalization, whereas the silicon analogue is actually destabilized.

E. Effect of Diffuse Functions. Numerous authors have recently considered the importance of adding diffuse functions to the basis set for calculations involving negative ions.[16] Most recently, Spitznagel and co-workers[16] have considered many anions and

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[13] These results are in concert with the NMR spectrum of the 1-methylsilacyclopentadienyl anion which gave no evidence for significant delocalization of negative charge: P. Boudjouk, B.-H. *Han*, and R. Sooriyakumaran, to be submitted.

[14] P. C. Hariharan and J. A. Pople, *Chem. Phys. Lett.*, **1972**, *16*, 217; M. S. Gordon, *Chem. Phys. Lett.*, **1980**, *76*, 163.

[15] J. A. Pople, J. S. Binkley, and R. Seeger, *Int. J. Quantum Chem., Quantum Chem. Symp.*, **1976**, *10*, 1.

[16] See, for example, G. W. Spitznagel, T. Clark, J. Chandresekhar, and P. v. R. Schleyer, *J. Comp. Chem.*, **3**, 363 (1982).

Table VII. Effect of Diffuse Functions on the Stability of $CH_3CH_2^-$ [a,b]

basis set[c]	ΔE	basis set[c]	ΔE	basis set[c,d]	ΔE[d]
STO-2G	5.1	3-21G	3.0	4-31G	2.1
STO-2G+ (0.017)	−8.4	3-21G+ (0.017)	−5.8	6-31G*	1.4
STO-2G+ (0.040)	−34.2	3-21G+ (0.04)	−11.1	4-31G+ (0.04)	−5.7
STO-2G++ (0.017)	−1.1	3-21G++ (0.017)	−2.4	6-31G*+ (0.04)	−4.0
STO-2G++ (0.040)	−6.3	3-21G++ (0.04)	−3.0	MP2/6-31G*+ (0.04)	−3.0

[a] Stability is measured by the reaction $CH_3CH_2^- + CH_4 \rightarrow CH_3^- + C_2H_6$. [b] Energies in kcal/mol. [c] Numbers in parentheses are exponents used for diffuse functions. [d] This column taken from ref 16.

Table VIII. Effect of Diffuse Functions on $C_5H_5^-$ [a]

	ΔE	
basis set[b]	$\alpha = 0.017$	$\alpha = 0.040$
π	63.8	72.3
p	73.0	89.1
s,π	71.7	84.8
s,p	75.4	93.1

[a] ΔE (in kcal/mol) refers to the bond-separation reaction. [b] Type of diffuse function added to the STO-2G basis set on each carbon.

the stabilizing or destabilizing effects of a variety of substituents. There is an important distinction to be made, however, between two types of anions. In the first, an extra electron is added to a stable, neutral molecule. This is similar to excitation into a Rydberg orbital and clearly requires appropriately diffuse basis functions for even a qualitative description of the process. One can also form an anion by simply removing a proton from the same stable, neutral molecule (e.g., Table VI). Qualitatively, the latter requires no new orbital description, but may require quantitative adjustments to accommodate the negative charge. Especially in the latter type of anion, the importance of diffuse basis functions is expected to diminish as the quality of the valence part of the basis set is improved.

To illustrate these effects, first consider the deprotonation of CH_4 to CH_3^-. Starting from STO-2G, diffuse s and p functions (exponent = 0.017[17]) lower the ΔE by 3.9 eV. Using the exponent suggested by Spitznagel et al. results in a further lowering of 1.5 eV. The corresponding lowerings starting from 3-21G are 0.8 and 0.3 eV, respectively. Similar results are found for ethane. Here, it also matters little whether one set of diffuse functions is placed at the midpoint of the CC bond (3-21G+) or at each carbon (3-21G++).

More pertinent with regard to the main point of the current work is the reaction, also consdered by Spitznagel et al., that measures the relative stability of $CH_3CH_2^-$:

$$CH_3CH_2^- + CH_4 \rightarrow CH_3^- + C_2H_6$$

The effect of diffuse functions on the ΔE for this reaction is analyzed in Table VII. The following points regarding this table are noteworthy: (1) With no diffuse functions, successive improvements in the basis set successively *reduce* ΔE toward zero, while the same improvements with diffuse functions in the basis set successively *increase* ΔE toward zero. The net result is only a small ΔE with or without the diffuse functions. (2) If the more diffuse exponent is used, one set of extra functions at the center is almost as effective as one set at each carbon. (3) for the split-valence basis set, the choice of which diffuse exponent is used is much less important. This is particularly true for 3-21G++.

A similar comparison for $C_5H_5^-$ is presented in Table VIII. To conserve computer time, these calculations, as well as those on the analogous silicon ring, were limited to STO-2G with diffuse functions. On the basis of the foregoing discussion, the use of larger valence basis sets will attenuate the results presented here. These results, then, must be regarded as an upper limit on the importance of diffuse functions. Regardless of exponent α, the major contribution to the aromatic character of the ring is, as expected, in the π space, although the σ effect is not negligible. Use of the more contracted functions ($\alpha = 0.04$[16]) gives a larger absolute energy lowering. These are the better choice in a variational sense and reduce the STO-2G ΔE (102 kcal/mol; see Table V) by about 9 kcal/mol. The most important conclusion, regarding this ring, that it is more aromatic than benzene, is therefore unchanged.

For silicon, an exponent of 0.04 was chosen since this is about the same as the exponent one would choose for the next most diffuse eventempered exponent.[18] For the silacyclopentadienyl anion, 0.04 has been used as the diffuse exponent for all heavy atoms. As found for the analogous carbon ring, the addition of diffuse functions here also diminishes the calculated bond-separation energy from 25 to 2 kcal/mol. If only diffuse π functions are included, ΔE is actually negative. Here again it is necessary to note that a larger valence basis set will certainly attenuate the effect of the diffuse functions.

Conclusion

The major conclusions which may be drawn from this work are as follows: (a) In contrast to silabenzene, which is nearly as "aromatic" as benzene, neither the silacyclopentadienyl anion nor the silacyclopropenyl cation appear to be as stabilized by delocalization effects. For the five-membered ring (predicted the valence basis sets to be approximately 25% as aromatic as the carbon analogue compared to the silabenzene molecule which is 80% as aromatic as benzene), this appears to result from the inability or disinclination of the silicon ring to redistribute the excess electron throughout the molecule. The increase in negative charge on the formal ionic center is much greater for Si than for C. The alternative, to distribute the negative charge onto the carbons, would presumably occur by increasing the double-bond character of C–Si and decreasing that of C–C. That this rearrangement is resisted is clear from the geometries in Table II. These conclusions are only slightly modified when diffuse functions are added to the basis set. The conclusion regarding the three-membered rings is based on the larger (3-21G) basis set. The latter predicts reactions D to be more exothermic than reaction E for X = Si. The reason for this behavior is less clear, but is probably related to increased strain relative to both the neutral silicon system and the carbon cation.

(b) The STO-2G basis set appears to provide a reliable measure of these effects, since geometries and relative energies are consistent with larger basis sets.

(c) The semiempirical INDO method may well be useful for predicting the structures of larger systems for which geometry optimizations even with STO-2G may be too time consuming.

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Registry No. Silabenzene, 289-77-0; cyclopropene, 2781-85-3; silacyclopropene, 67616-99-3; cyclopropenyl cation, 26810-74-2; silacyclopropenyl cation, 85883-40-5; cyclopentadiene, 542-92-7; silacyclopentadiene, 4723-64-2; cyclopentadienyl anion, 2143-53-5; silacyclopentadienyl anion, 85883-41-6; methane, 74-82-8; silane, 7803-62-5; ethane, 74-84-0; methylsilane, 992-94-9; ethyl anion, 2025-56-1.

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(17) M. S. Gordon and J. W. Caldwell, *J. Chem. Phys.*, **70**, 5503 (1979).

(18) M. W. Schmidt and K. Ruedenberg, *J. Chem. Phys.*, **71**, 3951 (1979).