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Molecular Structure and Bonding of a Silacyclopropane, Dimethyldispiro[bicyclo[4.1.0]heptane-7,2′-silacyclopropane-3′,7″-bicyclo[4.1.0]heptane]

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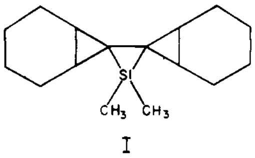
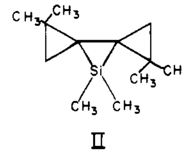
Abstract: The molecular structure of the first stable silacyclopropane compound has been determined and is compared with other three-membered ring compounds. CNDO calculations for C_2X heterocyclic ring systems demonstrate a decreasing C–X overlap population with increasing atomic number for a given periodic row. In addition, the enhanced stability associated with the dispiro structure in the silicon compound is confirmed as being due to increased C–X overlap population in the heteroring due to hyperconjugation bonding with the spiro cyclopropyl groups as previously suggested by Hoffmann. The compound exists with one cyclohexane ring folded towards the silicon atom and the other folded away. The silicon-ring carbon bond distance is 1.826 (3) Å and the carbon-carbon (heteroring) bond distance is 1.520 (3) Å. The structure of dimethyldispiro[bicyclo[4.1.0]heptane-7,2′-silacyclopropane-3,7″-bicyclo[4.1.0]heptane], $[(CH_3)_2Si(CC_6H_{10})_2]$, was determined from single-crystal x-ray data (2617 reflections) measured on a four-circle Picker x-ray diffractometer equipped with a graphite monochromator. The crystal system is triclinic with a = 10.225 (6) Å, b = 14.680 (9) Å, c = 6.544 (4) Å, α = 114.82 (5)°, β = 102.52 (4)°, and γ = 56.58 (3)°, with two molecules per unit cell and $\rho_{\text{calcd}} = 1.098$ g cm^{-3}. Least-squares refinement gave a final agreement factor of $R_w = 0.071$ and $R = 0.092$.

Three-membered ring compounds which contain two carbon atoms and one heteroatom have been the subject of extensive investigations over many years. Oxiranes, thiiranes, and aziridines have been known for a long time and have a well-developed chemistry. Phosphiranes are of more recent vintage and are much less stable than their oxygen, sulfur, and nitrogen analogues.[2] After having been sought for at least 25 years by various research groups, the first silacyclopropanes were prepared in 1972.[3] Initially, the only such compounds which were available were those in which the silacyclopropane unit was part of a dispiro system, i.e., I, II, and III. More recently, hexamethylsilacyclopropane also could be prepared and isolated.[4] Compounds I, II, and III, however, were much more stable thermally than hexamethylsilacyclopropane.

Structural studies have been carried out on oxiranes, thiiranes, aziridines, and phosphiranes. The C–C bond length in the C_2X ring has been found to vary with the stability of



I



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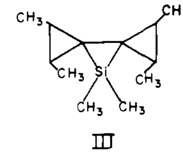
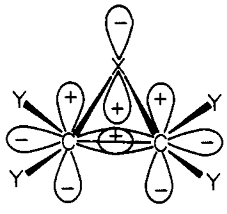
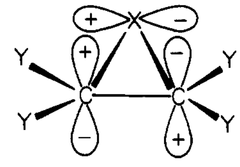


III

the b$_1\sigma$ molecular orbital[5] which has the symmetry indicated below. The donation of electrons from X into the anti-



$a_1\sigma(P_{\parallel})$
(p_z-p_x, p_z)



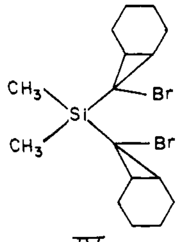
$b_1\sigma(P_{\parallel})$
(p_x-p_z)

bonding "π^*" orbital of the C–C moiety destabilizes the $b_1\sigma$ molecular orbital, with a concomitant increase in the C–C bond length and an increase in the angle, β, between the normal to the CY_2 planes and the C–C vector.[6b,c] It has been suggested that d orbitals may also be important in the stabilization of third-row heterocyclic compounds.[6a]

The purpose of this work is to compare the structural and bonding features of the three-membered ring heterocyclic compounds of the second- and third-row elements and, in particular, to present the first structural characterization of a silacyclopropane, dimethyldispiro[bicyclo[4.1.0]heptane-7,2′-silacyclopropane-3′,7″-bicyclo[4.1.0]heptane] (I), which is the only crystalline silacyclopropane which has been isolated thus far. The bonding in three-membered ring systems are compared via CNDO calculations[7] and the effects of internal and external ring substitution, including the dispiro configuration, are examined.

Experimental Section

A sample of dimethylbis(7-bromo-7-norcaranyl)silane (IV) was prepared by reaction of 7-bromo-7-lithionorcarane (in THF at −95°) with dimethyldichlorosilane as described previously.[3,8] Treatment of a THF solution of IV with an excess of magnesium at room temperature was followed by filtration of the reaction mixture and evaporation of the filtrate at reduced pressure. The residue was extracted with pentane, and the extracts were evaporated. The solid which remained was distilled (short path) at 95–97° at 0.01 mmHg to give a crystalline solid. The latter was recrystallized from pentane at −50°. After receipt at the University of Illinois, the sample was sublimed at 40° in a sealed tube. Several crystals were mounted and sealed under argon in thin-walled glass capillaries.



IV

All operations during the preparation, isolation, and handling of I must be carried out with rigorous exclusion of atmospheric oxygen and moisture since silacyclopropanes react exothermally with these reagents at room temperature. A crystalline sample of I will change to an oil irreversibly upon very brief exposure to the atmosphere.

Precession photographs showed no evidence of symmetry or systematic extinction indicating the space group $P1$ or $P\bar{1}$ in the triclinic crystal system. The space group $P1$ was assumed initially, but successful refinement of the structure favored the $P\bar{1}$ space group. A crystal measuring 0.50 × 0.35 × 0.35 mm was selected for data collection.

Fifteen reflections were carefully centered on a Picker four-circle diffractometer and lattice parameters obtained by least-squares refinement (T = 23°, λ 0.71069 Å). The final values obtained were a = 10.225 (6) Å, b = 14.680 (9) Å, c = 6.544 (4) Å, α = 114.82 (5)°, β = 102.52 (4)°, and γ = 56.58 (3)°. Due to the reactivity and solubility of the compound, accurate density measurements were not obtained. However, a density of 1.098 g cm^{-3}, calculated assuming two asymmetric units per cell, agrees with the rough density measurements that were made. Several ω scans showed the peaks to be asymmetric, indicating a slightly twinned crystal. The full peak width of 0.30° indicated an acceptable degree of mosaic spread for data collection.

Intensity data were measured on a fully automated Picker four-circle diffractometer equipped with a highly orientated graphite single-crystal monochromator using Mo Kα radiation. Data were measured using the θ-2θ scan technique with a scan rate of 1°/min, a takeoff angle of 1.6°, and a scan width of 1.7° being sufficient to collect all of the peak intensity. Stationary-background counts were measured for 10 sec before and after each peak. Three standards were measured every 50 reflections to ensure crystal and counter stability. The standard reflections showed no systematic change in intensity throughout data collection. A full sphere of data was collected, and the data were averaged to give a total of 2617 unique reflections ($2\theta_{max}$ = 50°), of which 1637 were considered to be observed using the criteria $I_{obsd} > 3\sigma_c(I)$. Here $\sigma_c = [T_c + 0.25(t_c/t_b)^2(B_1 + B_2)]^{1/2}$ where T_c is the total counts, t_c/t_b is the ratio of the time counting peak intensity to that spent counting backgrounds, and B_1 and B_2 are the background counts. The intensities were corrected for background and Lorentz and polarization factors and structure factor amplitudes were calculated using VANDY1, a local computer program. Due to the small linear absorption coefficient (μ = 4.83 cm^{-1}), no absorption correction was made. All reflections having a negative F_o were set equal to zero and given an arbitrary σ of 20. The structure solution and initial refinement were done using only observed reflections. Final refinement using the complete data set was carried out using counting statistical weights

Table I. Positional Parameters for Nonhydrogen Atoms in $(CH_3)_2Si(CC_6H_{10})_2$

Atom	x	y	z
Si	0.1986 (2)[a]	0.0698 (1)	−0.1705 (2)
C11	0.0852 (4)	0.2276 (3)	−0.1080 (5)
C12	0.0029 (4)	0.1629 (3)	−0.2568 (5)
C21	0.0348 (4)	0.3381 (3)	0.1022 (6)
C22	0.0984 (4)	0.3252 (3)	−0.1045 (6)
C23	0.2532 (5)	0.3149 (5)	−0.0994 (7)
C24	0.3554 (5)	0.2822 (5)	0.0953 (7)
C25	0.2632 (6)	0.3559 (5)	0.3139 (7)
C26	0.1351 (5)	0.3338 (4)	0.3119 (6)
C31	−0.0852 (4)	0.1620 (3)	−0.4754 (6)
C32	−0.1616 (4)	0.1868 (3)	−0.2669 (6)
C33	−0.3007 (5)	0.3050 (4)	−0.1587 (8)
C34	−0.3292 (6)	0.4008 (4)	−0.2345 (7)
C35	−0.3098 (5)	0.3603 (4)	−0.4790 (8)
C36	−0.1499 (4)	0.2590 (3)	−0.5648 (6)
C1	0.3377 (5)	−0.0282 (5)	−0.3711 (7)
C2	0.2198 (6)	0.0122 (5)	−0.0463 (8)

[a] Numbers in parentheses in all tables are estimated standard deviations of the least significant digits.

$$\sigma(|F|) = (|F|/2I)[T_c + 0.25(t_c/t_b)^2(B_1 + B_2) + (KI)^2]^{1/2}, \qquad K = 0.03$$

No significant systematic variation of $\omega(F_o - F_c)^2$ was seen with respect to $(\sin\theta)/\lambda$ or the magnitude of the structure factors. The C and Si scattering factors were taken from the tabulation of Cromer and Waber[9] and the hydrogen scattering factors from Stewart et al.[10] Anomalous dispersion corrections used for the silicon were those of Cromer and Liberman.[11]

Solution and Refinement of Structure. The structure was solved using the space group $P1$ by first placing a silicon atom at 0,0,0. A difference Fourier revealed a second silicon atom at 0.40, 0.14, −0.34. When these two silicon atoms were placed at −0.20, −0.07, 0.17 and 0.20, 0.07, −0.17, a difference Fourier revealed the 32 carbon atoms. The positions of the atoms in the two independent molecules indicated the correct space group to be $P\bar{1}$. The structure was refined[12] using isotropic thermal parameters to

$$R_1 = \sum ||F_o| - |F_c||/\sum|F_o| = 0.162$$
$$R_2 = (\sum w(F_o - F_c)^2/wF_o^2)^{1/2} = 0.170$$

A difference Fourier calculation revealed the positions of the hydrogen atoms. When the hydrogen atoms were included in the refinement, R_1 dropped to 0.138 and R_2 to 0.127. After converting to anisotropic temperature factors for the nonhydrogen atoms, and several cycles of full refinement of the nonhydrogen atoms and isotropic refinement of the hydrogen atoms using the full data set, the R factor converged to R_1 = 0.092 and R_2 = 0.071. A final difference Fourier revealed a residual density (0.7 e/Å^3) near the silicon atom and two areas (0.6 and 0.5 e/Å^3) near the end of the "exo" cyclohexane ring indicating some thermal disorder. The final positional parameters for the nonhydrogen atoms are given in Table I.

Table II. Interatomic Distances for Nonhydrogen Atoms

Atoms	Distance (Å)	Atoms	Distance (Å)
Si–C11	1.825 (3)[a]	C21–C26	1.528 (4)
Si–C12	1.827 (3)	C22–C23	1.500 (4)
C11–C12	1.520 (3)	C23–C24	1.528 (4)
Si–C1	1.856 (3)	C24–C25	1.507 (5)
Si–C2	1.859 (3)	C25–C26	1.510 (4)
C11–C21	1.518 (4)	C31–C36	1.518 (4)
C11–C22	1.501 (4)	C32–C33	1.491 (4)
C21–C22	1.525 (4)	C33–C34	1.543 (4)
C12–C31	1.517 (4)	C34–C35	1.473 (4)
C12–C32	1.509 (4)	C35–C36	1.490 (4)
C31–C32	1.530 (4)		

[a] Errors in lattice parameters are included in the estimated standard deviations.

Table III. Bond Angles for Nonhydrogen Atoms

Atoms	Angle (deg)	Atoms	Angle (deg)
C11–Si–C12	49.2 (1)[a]	C21–C22–C23	120.8 (2)
Si–C11–C12	65.5 (1)	C22–C23–C24	113.3 (2)
Si–C12–C11	65.3 (1)	C23–C24–C25	111.4 (3)
Cl–Si–C2	112.8 (1)	C24–C25–C26	112.1 (3)
C21–C11–C22	60.7 (2)	C25–C26–C21	112.9 (2)
C11–C21–C22	59.1 (2)	C36–C31–C32	119.5 (2)
C11–C22–C21	60.2 (2)	C31–C32–C33	119.3 (2)
C31–C12–C32	60.7 (2)	C32–C33–C34	114.6 (2)
C12–C31–C32	59.4 (2)	C33–C34–C35	113.1 (3)
C12–C32–C31	59.9 (2)	C34–C35–C36	113.2 (3)
C26–C21–C22	119.1 (2)	C35–C36–C31	114.8 (2)

[a] Errors in lattice parameters are included in estimated standard deviation.

Table IV. Dihedral Angles between Planes in $(CH_3)_2Si(CC_6H_{10})_2$

Plane 1	Plane 2	Dihedral angle (deg)
Si–C11–C12	Si–C1–C2	89.0
Si–C11–C12	C11–C21–C22	–87.8
Si–C11–C12	C12–C31–C32	–88.3
Si–C1–C2	C11–C21–C22	126.3
Si–C1–C2	C12–C31–C32	126.6
C11–C21–C22	C12–C31–C32	107.8

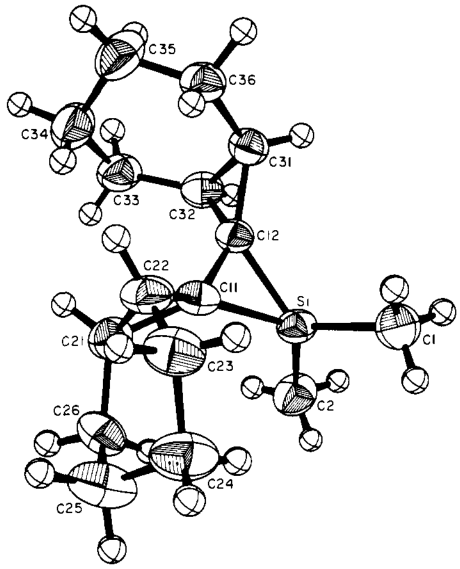


Figure 1. The molecular geometry of I showing the numbering system used.

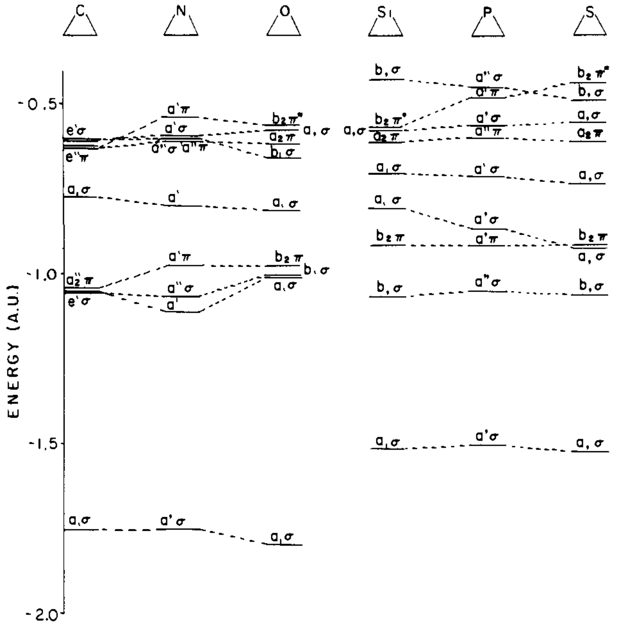
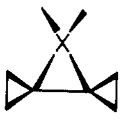


Figure 2. Correlation of the occupied molecular orbitals for the **unsub**stituted three-membered heterocyclic ring systems.

The anisotropic thermal parameters for the nonhydrogen atoms and the final positional and isotropic thermal parameters for the hydrogen atoms are given in the microfilm edition; see paragraph at end of paper regarding supplementary material. The bond distances, bond angles, and dihedral angles are given in Tables II, III, and IV. An ORTEP drawing of the molecule is given in Figure 1.

CNDO Calculations. The molecular coordinates used in the CNDO calculations were obtained using the known structures of cyclopropane,[13a] aziridine,[13b] oxirane,[13c] phosphirane,[13d] and thiirane[13c] and the dimethylsiladispiro[2.0.2.1]heptane fragment (Va)



Va x = Si

Vb x = C

obtained from the crystal structure. The C–C and C–Si bond distances in Va were averaged, and the carbon atoms placed at the appropriate positions without altering the dihedral angles. Hydrogen atoms were added using the known C–H bond distances for each type of carbon atom. For the carbon analogue, Vb, the ring size was reduced to conform to the bond distances in cyclopropane while the dihedral angles were maintained. In the hexamethyl compounds, the methyl groups were placed at appropriate distances and angles with the hydrogen positions added to maintain the C_{2v} or D_{3h} symmetry of the molecule. A correlation diagram of the filled molecular orbitals for the three-membered rings is given in Figures 2 and 3. The net atomic charges and overlap populations calculated for these structures are given in Table V.

Discussion

Structure. The molecule exhibits no internal symmetry since the potential mirror plane in the plane of the silacyclopropane ring is broken by the staggered configuration of the cyclohexane rings across this plane. One cyclohexane ring is folded towards the silicon atom, while the other ring is folded away from the silicon atom (Figure 1). The averaged C–C bond distances involving chemically equivalent carbon atoms in the cyclohexane and cyclopropane rings (Table VI) are comparable to those observed in other systems, with the thermal parameters of the carbon atoms increasing with increasing distance from the silacyclopropane rings. In addition, there is apparently a small amount of thermal disorder involving the carbon atoms C(34) and C(35). This can

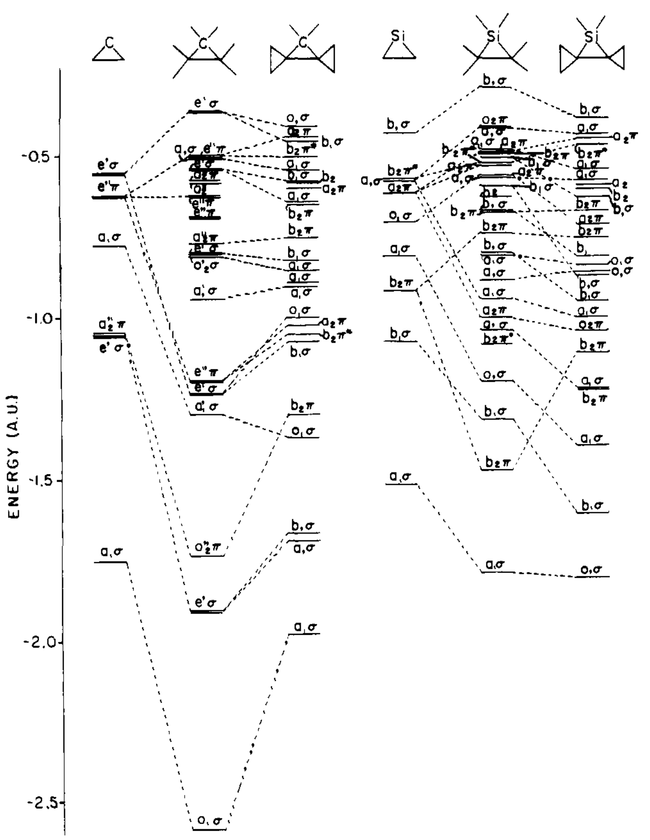


Figure 3. Correlation of the occupied molecular orbitals of the unsubstituted and substituted carbon and silicon compounds.

be attributed to molecular vibrational motion about the center of mass. The exocyclic Si-CH_3 bond distances (average = 1.858 (3) Å) are consistent with other structures.[14] The slight deviation from 90° in the dihedral angles between the silacyclopropane ring, the cyclopropane rings, and the silicon-methyl plane (Table IV) may be attributed to intramolecular nonbonding interactions involving the bulky cyclohexane rings.

The syn/anti relationship of the two spiroannelated norcaranylidene systems to the silicon atom is surprising since the syn/syn arrangement is expected on the basis of a concerted ring closure of the 1,3-dibromo compound (IV). It is possible that this isomer represents only a minor component of the reaction product. This could account for the fact that it was necessary to examine a large number of crystals to find a sample suitable for x-ray studies. A possible mechanism for the formation of the syn/anti form is described elsewhere.[15]

Comparison of C_2X Ring Systems. A comparison of bond lengths and bond angles for C_2X ring systems is given in Table VII. A decrease in the C-C bond distance from left to right is observed for both second- and third-row compounds. A plot of this distance vs. either the Mulliken orbital electronegativity (Figure 4) or the valence state ionization potential of the heteroatom[16] indicates that, as the Mulliken orbital electronegativity decreases, there is a corresponding lengthening of the C-C bond. This can be attributed to the heteroatom being able to donate more electron density into the π^* bond of the C-C fragment via the $b_1\sigma$ molecular orbital, which causes an increase in the C-C bond length. The C-X bond distances for X = carbon through oxygen systematically decrease, while the Si-C bond distance (1.826 (3) Å) is about the same as the S-C bond distance (1.819 (2) Å), but less than the P-C bond distance (1.867 (5) Å).

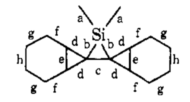
Table V. Net Atomic Charges and Overlap Populations[c]

Compound	Net atomic charge X	Net atomic charge C11,12		Overlap population[a] C–X	Overlap population[a] C–C
Cyclopropane	−0.018	−0.018		0.701	0.701
Aziridine	−0.167	+0.051		0.525	0.773
Oxirane	−0.194	+0.094		0.426	0.784
Silacyclopropane	+0.316[b]	−0.114[b]	s,p	0.338	0.887[b]
			d	0.205	
			T	0.543	
Phosphirane	+0.109	−0.055	s,p	0.159	0.928
			d	0.182	
			T	0.341	
Thiirane	−0.103	+0.003	s,p	0.181	0.925
			d	0.139	
			T	0.320	
Hexamethylcyclopropane	+0.173[b]	+0.173[b]		0.696	0.696
Vb	+0.034[b]	−0.035[b]		0.686	0.640
Hexamethylsilacyclopropane	−0.013[b]	+0.017[b]	s,p	0.258	0.822
			d	0.190	
			T	0.448	
Va	+0.130	0.000	s,p	0.277	0.860
			d	0.268	
			T	0.545	

[a] Milliken overlap populations using vectors transformed from CNDO orthogonal basis to overlapping basis. [b] Based on structure of I. [c] Key: s,p, overlap with only X's s,p orbitals; d, overlap involving only X's d orbitals; t, total overlap population.

Table VI. Averaged Chemically Equivalent Bond Lengths (Å)

a	1.858 (2)[a]
b	1.826 (2)
c	1.520 (3)
d	1.511 (8)
e	1.528 (4)
f	1.509 (17)
g	1.518 (22)
h	1.490 (24)

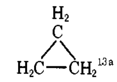
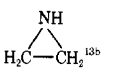
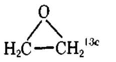
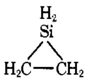
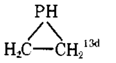
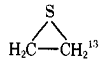


[a] Standard deviations computed from the deviations from the mean values, i.e., $S_X = [(\Sigma(X_1^2) - nx^{-2})/(n-1)]^{1/2}$.

The bonding schemes associated with $b_1\sigma$ (d_{xz}-p_z) and $a_1\sigma$ (d_{z^2}-p_x,p_z) are identical with the Dewar-Chatt model which has been used to describe the bonding in the metallocyclopropanes formed by the reactions of olefins with low valent transition metal compounds.[17,18] One might therefore expect some similarities in the structural features of the main group three-membered ring heterocycles and the transition metal-olefin systems. The main group analogy from a synthetic point of view is the interaction of an sp^2 hybridized carbene type of species (CH_2, SiH_2, PH, NH, etc.) with an olefin. As one example, the back-donation of electron density to the olefin π^* orbital through the $b_1\sigma$ molecular orbital should result in a lengthening of the C-C olefinic bond as compared to the free olefin and a bending of the olefinic substituents out of the olefinic plane which contains the C-C bond. Stalick and Ibers[6c] have observed that these two effects should be related to each other through a linear relationship between the "bent back" angle β and the C-C bond length, i.e., $\Delta\beta = 209(\Delta l)$ where $\Delta\beta$ is the change in the angle β defined as the angle between the normal to the CX_2 plane and the C-C bond. Δl is the change in angstroms in the central C-C distance of 1.339 Å. We note that a similar relationship holds for the main group cyclopropanes (Figure 5), i.e., as the C-C distance increases, the value of β decreases in agreement with a greater amount of electron density being donated into the olefin π^* orbital.

CNDO Calculations. The CNDO calculations on the C_2X ring systems can be compared qualitatively to examine the

Table VII. Comparison of Bond Lengths (Å) and Bond Angles (deg) for Heterocyclopropanes

	[13a]	[13b]	[13c]		[13d]	[13]
r(C–C)	1.510 (2)	1.480	1.472 (2)	1.520 (3)	1.502 (5)	1.492 (2)
r(C–H)	1.088 (3)	1.082	1.082 (2)	1.081^a	1.093 (5)	1.078 (2)
r(C–X)	1.510 (2)	1.488	1,436 (2)	1.826 (3)	1.867 (5)	1.819 (2)
r(X–H)	1.088 (3)	1.000	. . .	1.480^a	1.428 (5)	. . .
∠CXC	60.0	60.0	61.4	49.2 (1)	47.4 (5)	48.5 (1)
∠HCH	115.1 (10)	116.7	116.6 (1)	120.0^a	114.4 (5)	116.0 (1)
∠C–CH_2	150	159.4	159.5 (1)	143.9^a	149.5 (5)	151.7 (1)
∠HXC_2	117.6 (4)	112.0	. . .	120.0^a	95.7 (5)	. . .
∠XCC	60.0	60.2	59.2 (1)	65.4 (1)	66.3 (5)	65.8 (1)

^{a} Values used in CNDO calculations.

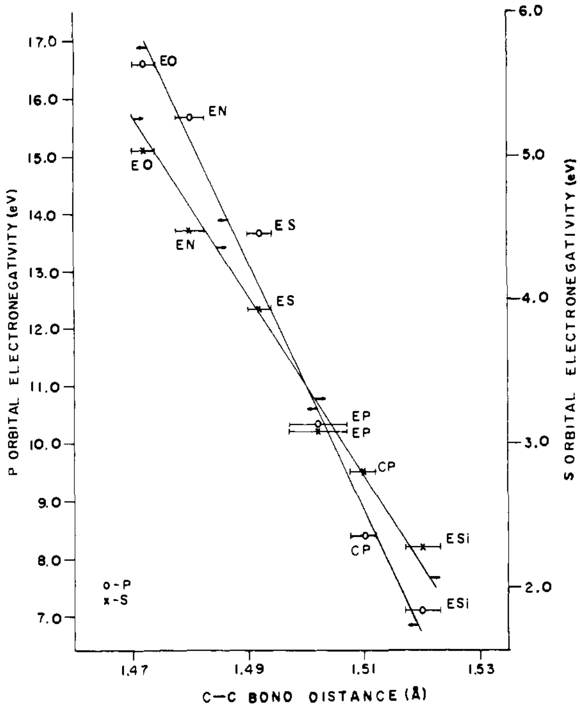


Figure 4. A plot of the S(X) and P(O) Mulliken orbital electronegativity, X_M, of the heteroatom vs. the C–C bond length (cyclopropane, CP; aziridine, EN; oxirane, EO; silacyclopropane, ESi; phosphirane, EP; and thiirane, ES). Values are from J. Thorhallsson, C. Fisk, and S. Traga, *Theor. Chim. Acta*, **12,** 80 (1968).

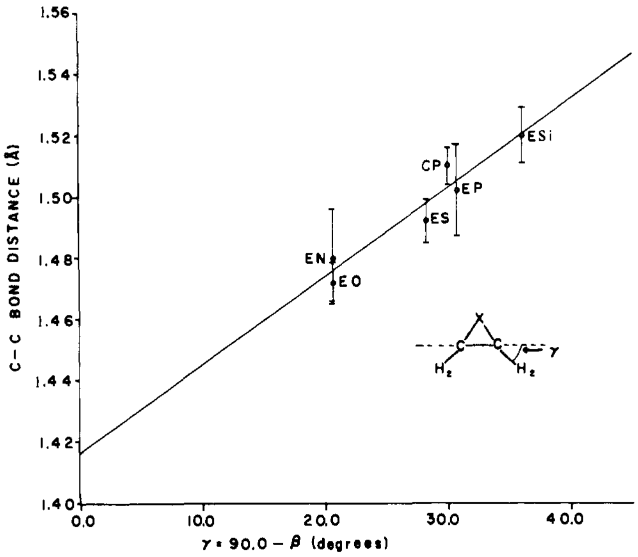
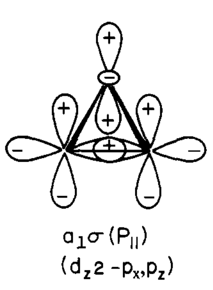
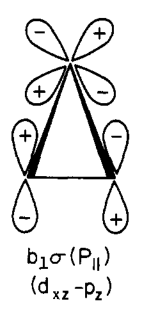


Figure 5. Plot of C-C bond distance vs. the bent back angle for the second- and third-row heterocyclopropanes (Cp, cyclopropane; EN, aziridine; EO, oxirane; ES, silacyclopropane; EP, phosphine; ES, thiirane).

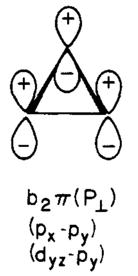
relative importance of the heteroatom and ring substitution on the stability of the three-membered ring. While second-row elements can only use s and p orbitals, the third-row elements can utilize the d_{z^2}, d_{xz}, and d_{yz} orbitals, which have the appropriate symmetry to form $a_1\sigma$, $b_1\sigma$, and $b_2\pi$ molecular orbitals, respectively, with the symmetry adapted carbon orbitals (see below). In the unsubstituted ring systems, the total overlap populations calculated for the X-C bond decrease systematically while the C-C overlap population increases with increasing atomic number for a given row in the periodic table (see Table V). In addition, the charge on the heteroatom becomes more negative with the electron density increasing in the s and p orbitals and decreasing in the d orbitals. The carbon atoms correspondingly become more positive as the electron density increases in the s and p_y orbitals and decreases in the p_x and p_z orbitals. This is due to the increasing electronegativity of the heteroatom and results in a shortening of the C-C bond as a result of less electron density in the C-C p_z-π^* orbital. This is evident in the energy level correlation diagram of the filled molecular orbitals for the C_2X ring system. As the heteroatom becomes more electronegative, the highest filled occupied MO changes from $b_1\sigma$ to $b_2\pi^*$, due to stabilization of the $b_1\sigma$ MO as described above and destabilization of the $b_2\pi^*$ MO as a result of lone pair electrons on nitrogen, oxygen, and sulfur which can interact (antibonding) with the p_y orbitals on the carbon atoms.



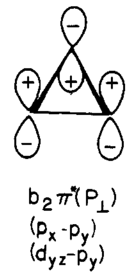
$a_1\sigma(P_{\parallel})$
$(d_{z^2}-p_x,p_z)$



$b_1\sigma(P_{\parallel})$
$(d_{xz}-p_z)$



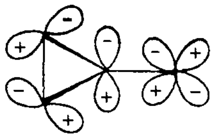
$b_2\pi(P_{\perp})$
(p_x-p_y)
$(d_{yz}-p_y)$



$b_2\pi^*(P_{\perp})$
(p_x-p_y)
$(d_{yz}-p_y)$

The large Si–C bond overlap population calculated for the unsubstituted and substituted silacyclopropane, based on the bond lengths determined for the substituted compound, is due primarily to the d orbital contribution, and in particular, it is the d_{yz} orbital on the silicon atom which has significantly more electron density (0.1638) than the d_{yz} orbital for phosphorus in phosphirane (0.0625) or for sulfur in thiirane (0.0440). This is associated with a short Si–C bond length and a substantially better overlap of the d_{yz} orbital with the ring carbon atom p_y orbital in the $b_2\pi$ molecular orbital. The net stabilization of $b_2\pi^*$ relative to $b_1\sigma$ in silacyclopropane as compared to thiirane is due to the lack of electron lone pairs on silicon.

In order to investigate the reason why the dispiro structure has been found able to stabilize the silacyclopropane ring, CNDO calculations were carried out on hexamethylsilacyclopropane and the dimethyldispirosilacyclopropane (Va) and their carbon analogues. Methyl substitution results in a marked decrease in the C–X overlap population and a removal of electron density from the ring carbon atoms. The dispiro structure increases the X–C overlap population from that observed in the unsubstituted compounds due to increased d orbital contributions. This increase can be attributed to the ability of cyclopropane rings to interact with adjacent π systems, or possibly low lying d orbitals on third-row atoms, through the use of the cyclopropane $b_1\sigma$ molecular orbital (see below).[19,20] This increases the electron density in the p_y orbital on the heterocyclic ring carbon atoms. It also is observed that the electron density in the other p orbitals on the ring carbon atoms decreases. The electronic charge on the methyl groups in the dispiro structure is more negative than for the corresponding Vb or hexamethyl structure. This could be due to the d_{yz} orbital accepting electron density from the carbon p_y orbital and in turn donating it to the methyl carbon atoms which are in the plane of the d_{yz} orbital. A correlation diagram of the filled molecular orbitals of hexamethylsilacyclopropane to Va shows that there is a large decrease (stabilization) in the energy for most of the molecular orbitals, especially the $b_1\sigma$ and $a_1\sigma$ orbitals. In support of the results of these calculations, we note that hexamethylsilacyclopropane has been found to be much less stable thermally than the dispirosilacyclopropane II. The latter has a half-life of about 7 days at 63° in THF solution, but the half-life of hexamethylsilacyclopropane under identical conditions is only 5 hr.[4]



$b_1\sigma - d_{xy}$

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Supplementary Material Available: anisotropic thermal parameters for the nonhydrogen atoms, positional parameters and isotropic thermal parameters, and structure factor tables for $(CH_3)_2Si(CC_6H_{10})_2$ (19 pages). Ordering information is given on any current masthead page.

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