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Electronic Structure of Thiirene and Silacyclopropene Substituted with Electropositive Groups

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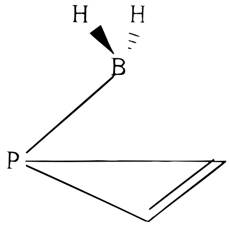
It has been revealed by ab initio calculations at various levels that electropositive substituents (Li, BeH, and BH_2) on silacyclopropene do not form bridge bond over the ring, as in the case of 1-BH_2-phosphirene. Although in 1-lithiumsilacyclopropene Li occupies a position on the top of the ring, this structure, however, should be more appropriately described as a silacyclopropene anion Li^+ ion pair, as shown by the MOs and Wiberg indices. For the various substituted thiirenes studied (with all combinations of the substituents Li, BeH, and BH_2), instead of having a hypervalent sulfur, bridge bond structures (over the CC bond) are formed in all cases. For BeH,BH_2-thiirene, the two substituents might position "above" or "behind" the ring, resulting in three different stable structures, and the most stable one has BeH forming a cage structure with the SCC ring. This bridge bond structure is similar to that in 1-BH_2-phosphirene. Except for the case of having two BH_2 groups, this cage structure has been found for all other substituent combinations. For this structure with two different substituent groups, the isomer with the more electropositive substituent group on the top of the ring is more stable. The bridge bond could be characterized by the participating AOs in both the highest doubly occupied a′ and a″ orbitals. Unlike in the case of 1-BH_2-phosphirene, where dynamic electron correlation was needed to stabilize the bridge bond structure, the MO interaction alone was shown to be enough for the stabilization of this structure for the substituted thiirenes considered in this work.

Introduction

In our previous work on 1-BH_2-phosphirene,[1] we reported that the BH_2 group occupies a bridging position on the top of the ring according to correlated ab initio calculations (Scheme l). This structure was shown to be stabilized by two factors from our calculations: the empty p orbital of boron, bridging over the otherwise antibonding π_2 MO of the ring, and dynamic electron correlation. Further studies on the phosphirene ring with BeH or Li, instead of the BH_2 group, resulted in similar structures[1] and not the usual opened form; however, these structures turned out to be saddle points on the potential surface according to second derivative calculations. Relaxing the C_s symmetry constraint, the ring opened up. This finding is in accord with experimental results, where it was found that the phosphirene ring opened up upon lithiation.[2] Calculations on the structure of 2-Li-cyclopropene at correlated levels also showed that the bridged structure reported at the HF/3-21G level previously[3] was not a true minimum. Nevertheless, the peculiar bonding in 1-BH_2-phosphirene mentioned initially has prompted us to further investigate how general this type of bonding could be for other three-membered ring systems.

In the present study, our attention is focused on some other substituted three-membered rings, containing heteroatoms, Si or S, belonging to the third row of the periodic table, which result in the silacyclopropene and the thiirene (with tetravalent S) rings as shown in Scheme 2. The substituents considered are Li, BeH, and BH_2. All of these groups have at least one vacant p orbital, which is needed[1] for the type of bonding being investigated in the present work. Thiirene itself has been subjected to several ab initio studies, which mainly aimed at obtaining harmonic vibrational frequencies[4] for spectral assignments, as well as gathering structural data.[4a,5] The protonation of the ring[6] and the relative stability with respect to isomeric molecules[7] have also been investigated by ab initio methods. Silacyclopropene and some related derivatives have been studied by ab initio calculations on a number of occassions[8−10] as well. However, to our knowledge, none of the substituent groups mentioned above have been considered with the three-membered rings of thiirene and silacyclopropene. We just note that both the edge and face complexes between Li^+ and cyclopropene have recently been investigated in a DFT (B3LYP/6-311+G**) and X-ray crystal structure study.[11] It was concluded that the edge complex was strongly favored, but a metastable Li^+ face complex was also permitted.

SCHEME 1: 1-BH_2-phosphirene



SCHEME 2: Substituted Silacyclopropene and Thiirene

Computational Details

From our previous study on 1-BH_2-phosphirene, electron correlation was found to be important in stabilizing the lowest

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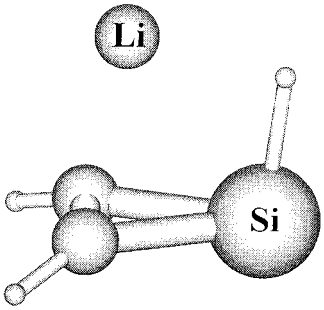

Figure 1. MP2/6-31G* optimized structure of 1-Li-silacyclopropene (see also Table 1), as shown by the MOLDEN program.[15]

energy structure. Therefore, the MP2/6-31G* level would be expected to be the lowest level required for this type of compounds. As will be discussed later, the minimum-energy structures obtained at the MP2/6-31G* level show the possibility of hydrogen bonds (C—H···X) in substituted thiirenes. As a result, geometry optimizations (and frequency calculations for some of the species studied; see later text) using a larger basis set, 6-31++G**, which would describe hydrogen bonds more adequately, were also carried out. In addition, HF/6-31G* calculations were carried out for comparison with the MP2 results in order to assess the importance of dynamic electron correlation effect in these compounds. CASSCF(8,8)/6-31G* optimization calculations were carried out to assess the importance of nondynamic electron correlation and hence the adequacy of the single reference correlation methods used in the present study.

All HF and some MP2 calculations were performed using CADPAC5.2,[12] and all CASSCF calculations, GAMESS-UK,[13] on the SG Power Challenge at Southampton, while some MP2 calculations were performed using GAUSSIAN 92[14] on the SG Indigo workstation at Budapest. In order to obtain consistent results from the two suites of programs (CADPAC and GAUSSIAN), the six-component Cartesian d functions were used and all electrons were active (no frozen cores) in the MP2 calculations, unless otherwise stated.

All calculations were performed with a C_s symmetry constraint and this was found to be adequate by the second derivative calculations for the mininum-energy structures obtained. Both optimization and frequency calculations were carried out at the HF and MP2 levels. For the MP2/6-31++G** calculations, however, the basis set used was found to have a few basis functions being close to linear dependence almost in all cases. In some cases, this led to scf convergence problem at some geometries. Consequently, geometry optimizations for some species studied have not reached the tight convergence criteria of having the maximum gradient of less than 10^{-5}, and frequency calculations have not been carried out for some of them. Nevertheless, all the MP2/6-31++G** structures reported here have the maximum gradient at the low 10^{-4} or below.The CASSCF(8,8)/6-31G** optimization calculations carried out in this study have a configurational space of ca. 900 configurations in all cases.

Results and Discussion

Silacyclopropenes. In the silacyclopropene series, the BeH and the BH_2 substituents occupy the generally expected opened position, with the near tetrahedral angles about silicon as shown in Scheme 2 (some essential structural data are given in Table 1). 1-Li-silacyclopropene, however, has a pyramidal SiC_2Li structure (with both Li and the H atom bonded to Si on the same side of the ring; see Figure 1 and Table 1) at all levels of the theory considered here. Similar structures have recently been reported for the five-membered rings of lithium silolide[16] and dilithiumsilole[17] at the MP2/6-1+G* level. For this lithiated compound, the structural characteristics of the ring differs from that of the other derivatives, as shown by the SiC bond length, which elongates by about 0.12 Å in comparison with the HBe and H_2B derivatives. The best description of this structure can be given basically as a Li^+ and a silacyclopropene$^-$ ion pair. The Wiberg indices[18] (HF/6-31G*//MP2/6-31G*) are in agreement with this description, since all LiSi and LiC Wiberg indices are less than 0.05, while in case of HBe- and H_2B-silacyclopropenes the Si−Be and Si−B Wiberg indices are significantly larger (see Table 1). The structural characteristics of the Li derivative (for example the OOP of H_{Si}, the angle defined by the middle of the CC, Si, and H_{Si}, is near 90°; see Figure 1) of the SiC_2H_3 part of the system are similar to those of phosphirene (PC_2H_3). This behavior is not surprising since P is isoelectronic with Si^-. Indeed, from the calculations on the phosphirene Li^+ complex at the HF/6-31G* level, a similar structure to that of 1-Li-silacyclopropene has been obtained. The SiC Wiberg indices in 1-Li-silacyclopropene are significantly smaller than those of the other two derivatives, in accordance with the lengthening of the corresponding two bonds. This behavior might be related to some antiaromatic character in the silacyclopropene anion. The uppermost occupied MOs of 1-Li-silacyclopropene do not show the participation of unoccupied Li orbitals, such as in the case of 1-BH_2-phosphirene.[1] The LUMO is mainly a Li s orbital, in accordance with the ionic description of the system. Therefore, although the structural position of Li might suggest some sort of ionic bridge bond in silacyclopropene (cf the face complex of Li^+ in cyclopropene[11]), we conclude that this is not the kind of bridge bond (due to MO interaction) we look for as in 1-BH_2-phosphirene.

Since none of the silacyclopropenes exhibited the unusual bridge bond, it seems that a ring heteroatom with higher electronegativity and/or more lone pair orbital is required to stabilize this type of bonding. The most obvious candidate would be S. However, the replacement of P in phosphirene by S gives thiirene, which would have no possibility of having further substituents on sulfur, unless in a hypervalent form. This would lead to a more complex bonding situation and hence would also be more interesting.

Thiirenes. The representative results are summarized in Tables 2−4. The geometry optimization and frequency calculations give the following minima (with all real vibrational frequencies) for the various substituent combinations: For BeH,-BH_2-thiirene, there are three prototype structures (**a**, **b**, and **c**), as shown in Figure 2. Structure **a** is the most stable (see Table 4 for the major structural and energy differences for the three structures). It has a cage structure formed with one substituent and the ring, similar to that in 1-BH_2-phosphirene, while the other substituent forms a bridge bond over CC on the opposite side of the ring (but outside; Figure 2, structure **a**). For all other substituent combinations, this cage structure **a** has been located as minima, except for BH_2,BH_2-thiirene (to be discussed later). When having two different substituent groups, structure **a** can have two isomers with different substituents positioned on the top of the ring forming the cage structure (except for BH_2 which does not form a cage structure in all cases; see later text). Both isomers are true minima, but the isomer with the more electropositive group on the top of the ring is always more stable (see for example Table 3). For Li,BH_2-thiirene, other than structure **a**, structure **b** has also been obtained as a minimum, but is 40.7 kcal·mol^{-1} higher in energy than structure **a** at the MP2/6-31G* level. It seems likely that all three structures **a**, **b**, and **c** are minima on the energy surfaces for

TABLE 1: Optimized Structural Parameters[a] and Total Energies (in au) Obtained at Different Levels of Calculation for the Lowest-Energy Structures[b] of the 1-H,X-silacyclopropenes, Where X = Li, BeH, BH_2

substituent on Si	HF/6-31G*	CASSCF/6-31G*	MP2/6-31G*	MP2/6-311+G*	I_{wib}[c]
H,Li-	−373.75230	−373.81072	−374.12250	−374.33497	
SiLi	2.515	2.510	2.495	2.470	0.04
SiC	1.945	1.954	1.971	1.968	0.69
CC	1.322	1.341	1.336	1.339	2.03
OOP[d]	55.6	55.1	54.9	54.7	
H,BeH-	−381.51578	−381.58426	−381.90459	−382.11132	
SiBe	2.203	2.214	2.165	2.167	0.66
SiC	1.831	1.873	1.854	1.854	0.85
CC	1.315	1.329	1.328	1.332	2.01
OOP	124.9	124.6	122.2	121.4	
H,BH_2-	−392.13230	−392.20670	−392.56121	−392.59680[e]	
SiB	2.034	2.004	1.989	1.991	0.98
SiC	1.811	1.864	1.850	1.853	0.84
CC	1.326	1.328	1.325	1.330	2.00
OOP	126.7	124.2	121.9	121.3	

[a] Bond lengths in angstroms. [b] For Li, see Figure 1; for BeH and BH_2, see Scheme 2. [c] The Wiberg index is at the HF/6-31G*//MP2/6-31G* level. [d] OOP is defined as the angle (in degrees) formed by the substituent, Si and the middle point of the CC bond. [e] MP2(FC) and five-component d functions were employed in this calculation.

TABLE 2: Some Optimized Bond Lengths (in Å) and the Total Energies (in au) Obtained at Different Levels of Calculation for the Lowest-Energy Structure[a] of the X,Y-thiirene Series, Where X,Y = Li, BeH, and/or BH_2

X,Y-	HF/6-31G*	CASSCF/6-31G*	MP2/6-31G*	MP2/6-31++G**
Li,Li-	−489.22025	−489.28737	−489.65903	−489.69168
SLi	2.1887, 2.5462	2.2108, 2.5297	2.2041, 2.5084	2.1970, 2.5201
SC	1.9635	1.9724	1.9103	1.9082
CC	1.4617	1.4673	1.4801	1.4817
Li,BeH-	−497.00225	−497.05770	497.47143	−497.50795
SLi	2.2085	2.2291	2.2194	2.2137
SBe	2.6792	2.6837	2.6122	2.6363
SC	1.8842	1.9100	1.8680	1.8649
CC	1.4796	1.4829	1.4970	1.5015
Li,BH_2-	−507.62544	−507.70377	−508.14361	−508.18192
SLi	2.2341	2.2561	2.2468	2.2422
SB	2.7200	2.7461	2.7126	2.7109
SC	1.8442	1.8811	1.8413	1.8380
CC	1.4679	1.5057	1.4825	1.4845
BeH,BeH-	−504.74434	−504.79247	−505.25526	−505.29773
SBe	1.9490, 2.7058	1.9861, 2.7448	1.9576, 2.6651	1.9623, 2.6878
SC	1.8881	1.9210	1.8697	1.8680
CC	1.4932	1.5441	1.5159	1.5196
BeH,BH_2	−515.37202	−515.43087	−515.92392	−515.97548
SBe	1.9684	2.0159	1.9780	1.9823
SB	2.7264	2.7508	2.7269	2.7259
SC	1.8492	1.8930	1.8447	1.8438
CC	1.4844	1.5025	1.5011	1.5024
BH_2,BH_2-	−525.97860	−526.04812	−526.55223	−526.61313
SB	1.8233, 2.6907	1.8297, 2.6909	1.8109, 2.6371	1.8128, 2.6366
SC	1.9352	1.9377	1.8813	1.8781
CC	1.4189	1.4527	1.4330	1.4350

[a] All structures are that represented by structure **a**, except for BH_2,BH_2-, which is structure **b** (see Figure 2 and text).

most substituent combinations (with perhaps the exceptions which have already been mentioned). However, an attempt has not been made to locate all three structures **a**, **b**, and **c** for all substituent combinations, because it is felt that the three structures of BeH,BH_2-thiirene obtained would be representative of the rest, and attention should be focused on the lowest-energy structures/isomers of the series. Since the primary interest in this work is on the stabilization by the substituent in forming the type of bridge bond and cage structure with three-membered ring systems similar to that in 1-BH_2-phosphirene, structure **a** is the most important. Nevertheless, some general structural considerations, which may also help us to understand the structural stability of the system, are given in the following.

All structures presented in Tables 2−4 have the common structural characteristics that the substituent groups form at least one bridge bonds over CC. In the case of the structures **a** and **b**, the substituents occupy a trans position. For structure **a**, it is clear that one of the substituents (shorter distance to S) forms a bridge bonded cage with the SCC ring, while the other substituent does not (as it is outside the ring; see Figure 2). For structure **b**, it seems that a cage structure does not exist, as the substitutent with a shorter distance to S (SB = 1.7974 Å; see Table 4 and Figure 2) is rather far away from the C atoms (BC = 2.7761 Å). The MOs also do not reveal any bridge bond interaction involving this substituent group. Structure **c** is always the least stable one among the three structures (Table 4). It can be described as having two bridge bonds over the CC bond. Such structures were reported to be minima on the $C_2H_2Li_2$ potential energy surface.[19] (Note that, describing the bonding in three-membered rings, a dative bonded structure was

TABLE 3: Some Geometric Parameters and Essential Characteristics of the Two Cage Structures[a] of Li,BeH-SC2H2 at the MP2/6-31G* and MP2/6-31++G Level**

	Li cage		Be cage	
MP2/	6-31G*	6-31++G**	6-31G*	6-31++G**
Sli	2.2194	2.2137	2.6825	2.6814
Sbe	2.6122	2.6363	1.9561	1.9591
SC	1.8680	1.8649	1.8982	1.8994
CC	1.4970	1.5015	1.4986	1.4983
LiC	2.1600	2.1451	1.9663	1.9519
BeC	1.7250	1.7281	1.8593	1.8632
XH[b]	2.0180	1.9935	1.7113	1.7109
charge/e				
S	0.12	0.11	0.09	0.08
CH	−0.17	−0.43	−0.14	−0.08
Li	0.22	0.33	0.30	0.08
BeH	0.00	0.43	−0.10	0.01
lowest freq/cm^{-1}	135.2	*c*	152.9	*c*
orbital energy/au				
a′ HOMO	−0.3242	−0.3363	−0.3589	−0.3611
a″ HOMO	−0.3248	−0.3291	−0.3130	−0.3158
total energy/au	−497.47143	−497.50795	−497.45737	−497.49569
rel energy/kcal mol^{-1}	0.0	0.0	8.7	7.7

[a] Both cage structures are of structure type **a**, but with different substituent groups forming the bridge bond in the cage. [b] X refers to the substituent in the cage and XH is the bond distance between X and the H bonded to C; note that XH is shorter than XC in all cases (see text). [c] Basis functions near linear dependence, frequency calculations not carried out (see text).

TABLE 4: Some Geometric Parameters (Bond Lengths in Å) and Important Characteristics of the Different Isomeric Structures (a, b, and c)[a] of BeH,BH$_2$-SC$_2$H$_2$ at the MP2/6-31G* Level

	isomer **a**	isomer **b**	isomer **c**
SBe	1.9781	2.6207	2.6359
SB	2.7269	1.7974	2.6871
SC	1.8447	1.8863	1.8325
CC	1.5011	1.4532	1.5125
BC	1.6207	2.7761	1.7357
BeC	1.8628	1.7487	1.7443
BeH[b]	1.8583	2.7736	2.7354
BH[b]	2.5338	2.7544	1.6264
charge/e			
S	0.14	0.17	0.07
CH	−0.16	−0.18	−0.17
BH$_2$	0.04	0.07	0.10
BeH	0.14	0.11	0.17
lowest freq/cm^{-1}	279.7(a″)	120.6(a″)	120.6(a′)
orbital energy/au			
a′ HOMO	−0.4049	−0.3973	−0.3620
a″ HOMO	−0.4240	−0.3491	−0.3728
total energy/au	−515.92392	−515.88122	−515.85984
rel energy/kcal mol^{-1}	0.0	26.8	40.2

[a] See text and Figure 2. [b] These are refered to the HX distances in C—H···X; see text.

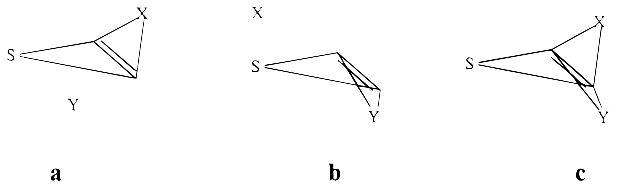

Figure 2. The **a**, **b**, and **c** type structure of BeH,BH$_2$-thiirene (see text and Table 4).

suggested by Grev and Schaefer.[20]) Obviously the bridge bond over the CC bond plays an important role in all structures considered in this work (including even structures **a** and **b**). The fourth possible structure, with both substituents forming bridge bonded cages on opposite sides of the ring, had been attempted, but rearranged to structures **a**−**c** during the geometry optimization in all cases.

Focusing on structures **a**, it has been mentioned that it shows the preference of having the more electropositive group to occupy the bridging position over the ring. This behavior is in accord with the expected participation of the unoccupied orbital of the substituent in a bridge bond. With a more electropositive substituent, its LUMO is more stabilized, allowing increased interaction and stabilization with the occupied orbitals of the ring. This kind of bonding interaction, perhaps, may be considered as similar to 1-BH$_2$-phosphirene.[1] However, if the high-lying occupied orbitals were inspected, it could be seen that, in contrast to 1-BH$_2$-phosphirene, where the stabilization comes from the HOMO (of a′ symmetry), for structure **a** of the substituted thiirenes considered here, stabilization comes from two highest-lying occupied orbitals (for the sake of simplicity, these are denoted as HOMOs from now on) of a′ and a″ symmetry. For both of these HOMOs, the vacant p orbitals of the substituent group of the respective symmetries are responsible for changing the otherwise antibonding combination of the ring-localized orbitals into overall bonding combinations. These two HOMOs are rather delocalized. The HOMO of a′ symmetry in the BeH,BH$_2$ derivative (structure **a** presented in Figure 2) is shown in Figure 3 as representative of this type of bonding interaction. This orbital is antibonding between the CC π-bond and the S lone pair, as should be in unsubstituted thiirene, but it is considerably different below and above the SCC plane with the participation of the Be unoccupied p orbital, which has now changed the interaction to an overall bonding one. This MO has similar characteristics to the HOMO of 1-BH$_2$-phosphirene (also of a′ symmetry). The involvement of

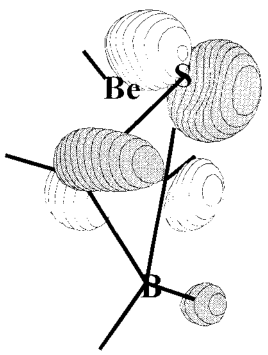

Figure 3. The a′ HOMO of the a type structure of BeH,BH$_2$-thiirene, at its MP2/6-31G* geometry as shown by the MOLDEN program.[15] Orbital contour was given at 0.1 au.

the empty Be p orbital should contribute to the stabilization of the CS bond. Indeed, there is some decrease of this bond length with respect to diborothiirene (0.03 Å at MP2/6-31++G*), or to the structure **b** of the BeH,BH_2 derivative. A similar kind of bonding stabilization can also be observed for the HOMO of a″ symmetry. The relative ordering of these two HOMOs of a′ and a″ symmetries in substituted thiirenes is very much case dependent, with no obvious trends being observed. Nevertheless, their orbital energies are very close as shown in Tables 3 and 4, suggesting that probably both HOMOs are as important in considering the bonding stability in these compounds. The exceptional structural behavior of BH_2,BH_2-thiirene, which is to be discussed in the following, also supports this conclusion.

With the BH_2 group, the situation for substituted thiirenes is quite different to that in 1-BH_2-phosphirene. For the former, the BH_2 group is always in the symmetry plane of the molecule, in contrast to the structure observed for l-BH_2-phosphirene, where it is in a plane perpendicular to the molecular plane containing the three-membered ring.[1] (For substituted thiirenes involving the BH_2 group, when the BH_2 group is in a perpendicular plane, the optimized structure was found to be a saddle point with one imaginary frequency in all cases.) With the former arrangement, the empty p orbital of boron, having a″ symmetry, is involved in the formation of the two-electron three-center bond over CC (a″ HOMO), but cannot be involved in the bridge bond above the ring (a′ HOMO; Figure 3). It seems that, for substituted thiirenes with the BH_2 group, the stabilization interaction in the a″ HOMO is preferred over that in the a′ HOMO, resulting in having the BH_2 group in the symmetry plane. In addition, with two BH_2 groups, no cage structure formed by the bridge bond over the top of the three-member ring could be located (only structure **b** was located), and for a more electropositive substitutent in combination with BH_2, the former is always the one forming the bridge bond over the ring, while BH_2 is outside the ring. All the above observations and considerations suggest that the cage structure in substituted thiirenes requires stabilization in both the a′ and a″ HOMOs by the two vacant p orbitals (a′ and a″ symmetry, respectively) of the substituent.

Since B in BH_2 only one vacant p orbital, stabilization by it on one HOMO, whether of a′ or a″ symmetry, seems to be insufficient to form a cage structure.

To investigate the reliability of the MP2/6-31G* level, HF/6-31G*, MP2/6-31++G*, and CASSCF(8,8)/6-31G* calculations were carried out for the most stable structure of all substituent combinations (structure **a** for all, except for BH_2,BH_2-thiirene, which is structure **b**). The results are summarized in Table 2. Comparing the optimized structures obtained at different levels, they are essentially the same structure. This is in contrast to l-BH_2-phosphirene, where dynamic electron correlation is required to stabilize the bridge bonded cage structure and for it to become of the lowest energy. Although the CASSCF calculations gave slightly longer bond lengths than both the HF and MP2 calculations, the computed CI coefficients show that there is only one dominant configuration (with a CI coefficient of larger than 0.92), which is the HF configuration, in all cases. At the same time, the MP2/6-31++G** results are almost identical to the MP2/6-31G* results. All these observations suggest that these structures can be adequately described even by the HF/6-31G* level of theory. We just note that the wave functions (MOs) obtained at the CASSCF/6-31G*, MP2/6-31G*, and MP2/6-31++G** levels differ somewhat. In the latter case, the diffuse functions have significant contributions to some occupied MOs. It should also be noted that, for structure **a**, the XH distances, where X is the heavy atom of the substituent group which forms the cage structure with the three-membered ring, and H is the hydrogen atom bonded to C (Table 3 and 4), are shorter than the XC distances in all cases and at all levels of calculation. This may suggest the involvement of H in the C—H···X interaction, or a certain degree of hydrogen bonds. Nevertheless, the better description of the H atoms by the 6-31++G** basis has not changed the results to any significant extent as mentioned above (Tables 2 and 3).

Considering the possibility of hypervalent sulfur in the cage structure, although the SX and CX bond lengths in the SC2X cage structure, and even the CC bond length, are comparable in some cases (such as isomer **a** in Table 4), the present bonding situation is probably far from a hypervalent sulfur picture, where two axial substituents above and below sulfur would normally be expected (see Scheme 2; note that no such structure as shown has been located by the geometry optimization as a stationary point). This conclusion is supported by the computed Wiberg indices. For example, for the BeH,BH_2 derivative, although the SBe distance is not too large (1.957 Å), the Wiberg bond index[18] is only 0.263, suggesting that the bonding is mainly ionic. This is understandable, considering that hypervalent bonds are usually stabilized by electronegative, but not electropositive groups in the axial position.[21] Considering other bonds of the cage structure, the Wiberg bond indices, for example, of the BeH,BH_2 derivative show essentially single bonds between SC (0.955) and CC (0.998), while somewhat weaker than single bond is between B and C (0.718). The Wiberg index between C and Be is only slightly larger than zero, despite the expectations based on the shapes of the two HOMOs discussed above. It should be noted, however, that the interaction between the Be unoccupied in-plane p orbitals and the π-cloud of the CC bond occurs in the middle of the CC bond in the a′ HOMO, while for the a″ HOMO, there is a nodal plane through the Be and S atoms (and the CC bond). For such kind of delocalized bonding interaction, probably its interpretation based on the Wiberg bond indices should be viewed with caution. Perhaps, an alternative description of this cage structure may be an ion pair of l-thia-3-borobicyclobutane anion and BeH^+. A similar structure (l-phosphino-3-borobicyclobutadiene) was more stable than l-BH_2-phosphirene on the potential energy surface.[1] There are, however, some notable differences between the present structure and l-phosphino-3-borobicyclobutadiene. In the present case an adequate description of the electronic structure could be given even at the HF level, but l-phosphino-3-borobicyclobutane could properly be treated at the MCSCF level only, where two configurations should have been taken into consideration. One of them could be related to the two annulated three-membered rings, while the other one to the four-membered ring with two somewhat coupled π-electrons on the carbon atoms. In the present case the first description is dominant, as it can be seen on the CC bond length, which is somewhat smaller than the normal single bond distance. The CC distance in 1-phosphino-3-borobicyclobutadiene is 1.625 Å at the MP2/6-31G* and 1.713 Å at the CASSCF/6-31G* level.

Conclusions

In a search for three-membered ring compounds stabilized by a bridge bond of an electropositive substituent, it turned out that in the case of silacyclopropenes, although Li occupies a position on the top of the ring, this structure is more appropriately described as having an ionic structure according to the Wiberg bond indices, rather than having the kind of bridge bond observed in 1-BH_2-phosphirene to be due to MO interaction. With the other two substituents, BeH and BH_2, only the open form structure (Scheme 2) was obtained.

Among thiirenes, however, most substituent combinations were found to give stable cage structures, in which Li or Be occupies a bridging position above the three membered ring. In the case of having two different substituent groups, the more electropositive one would be prefered to form the bridge bond and this structure is always the most stable among the possible isomeric forms (**a**−**c**). The bridge bond structure was, however, not formed with BH_2, contrary to our previous finding for the phosphirene three-membered ring. The reason for this observation is probably because there is only one vacant p orbital available in B (of BH_2) for the stabilization of the otherwise antibonding HOMO, but two vacant p orbitals from the substituent are required to stabilize both the a′ and a″ HOMOs of the cage structure in substituted thiirenes.

The overall description of the bonding interaction in the cage structure of substituted thiirenes is rather complex: The a′ and a″ HOMOs show delocalized interaction above and below the three-membered ring involving the respective vacant p orbitals of the substituent. Wiberg indices suggest ionic interaction and possibly an ion pair (for the substituent involving in the cage structure). However, charge densities obtained by the Mullikan population analysis (Tables 3 and 4) suggest less ionic interactions in the system than the Wiberg bond indices. Nevertheless, both the Wiberg bond indices and structural considerations indicate that a hypervalent sulfur description is probably inappropriate. In addition, structural considerations suggest a possibility of hydrogen-bonding interaction. Above all, it seems clear that thiirene has a much richer chemistry with electropositive substituents than phosphirene and silacyclopropene and that bridge bonded cage structures could be formed more readily with thiirene than with the relatively more electropositive counterparts. The most important conclusion is that the cage structure in thiirenes is stabilized in both the a′ and a″ HOMOs by the vacant p orbitals of the electropositive substituent.

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