

Theoretical Study of Bicyclo[2.2.0]hexaplumbane. A More Flexible and Less Strained Pb Skeleton compared with C, Si, Ge, and Sn Skeletons

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Ab initio calculations predict that bicyclo[2.2.0]hexaplumbane is less strained than its lighter analogues and prefers C_2 to C_{2v} symmetry, but the energy difference between C_2 and C_{2v} is remarkably small despite the considerable geometrical differences.

The preparation and characterization of the heavier group 14 analogues of bicyclo[2.2.0]hexane (**1**) are of considerable importance in the design of new materials, the ladder polymetallanes. We have calculated the properties of bicyclo[2.2.0]hexasilane (**2**)¹ and bicyclo[2.2.0]hexagermane (**3**).² In the last two years the first synthetic and *X*-ray structural studies have been made of a derivative of (**2**).^{3,4} Although the germanium analogues have not as yet been subjected to experimental tests, a bicyclo[2.2.0]hexastannane (**4**) derivative was synthesized recently as the first tin example and its *X*-ray structure was determined.⁵

In view of the experimental advances, we now report an *ab initio* prediction of the structure and strain of the still heavier lead analogue, bicyclo[2.2.0]hexaplumbane (**5**). Geometries were fully optimized at the Hartree-Fock (HF) level with the *ab initio* relativistic effective core potentials⁶ by using the double-zeta (DZ) and DZ + d basis sets⁶ augmented by a set of six d-type polarization functions (exponent 0.164)⁷ on Pb: the basis set used for H is of DZ quality.⁸ For a systematic comparison, (**2**)—(**4**) were also calculated at the HF/DZ and HF/DZ+d levels with d exponents of 0.262 (Si), 0.246 (Ge),

and 0.183 (Sn),⁷ while (**1**) was calculated at the HF/3-21G and HF/6-31G* level.⁹

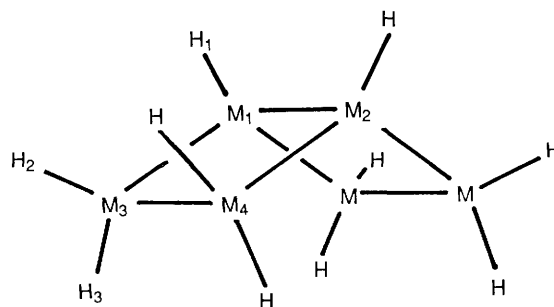


Figure 1. The C_{2v} structures of bicyclic compounds [M = C (**1**), Si (**2**), Ge (**3**), Sn (**4**), and Pb (**5**)]. The HF/DZ+d (HF/DZ) total energies of (**2**)—(**5**) are -28.42140 (-28.22774), -27.69617 (-27.57098), -25.30672 (-25.22740), and -25.67965 (-25.64281) a.u., respectively. The HF/6-31G* (HF/3-21G) total energy of (**1**) is -232.96555 (-231.67441) a.u.

Table 1. Optimized geometrical parameters in Å and degrees at the HF/DZ and HF/DZ+d levels.^a

	C (1) ^b		Si (2)		Ge (3)		Sn (4)		Pb (5)	
$r(M_1M_2)$	1.559	(1.588)	2.389	(2.401)	2.527	(2.528)	2.883	(2.870)	2.934	(2.916)
$r(M_1M_3)$	1.545	(1.560)	2.365	(2.371)	2.506	(2.501)	2.865	(2.848)	2.919	(2.899)
$r(M_3M_4)$	1.552	(1.574)	2.369	(2.374)	2.509	(2.500)	2.869	(2.848)	2.915	(2.895)
$r(M_1H_1)$	1.083	(1.077)	1.478	(1.475)	1.543	(1.538)	1.716	(1.707)	1.747	(1.739)
$r(M_3H_2)$	1.084	(1.082)	1.479	(1.476)	1.544	(1.538)	1.716	(1.709)	1.744	(1.736)
$r(M_3H_3)$	1.085	(1.081)	1.478	(1.476)	1.543	(1.538)	1.716	(1.708)	1.744	(1.736)
$\angle M_1M_2M_4$	89.9	(89.7)	89.8	(89.7)	89.8	(89.7)	89.9	(89.8)	89.8	(89.8)
$\angle M_1M_3M_4$	90.1	(90.3)	90.2	(90.3)	90.2	(90.3)	90.1	(90.2)	90.2	(90.2)
$\angle M_2M_1H_1$	123.3	(123.8)	125.1	(124.8)	125.0	(124.9)	124.7	(124.7)	124.6	(124.4)
$\angle M_1M_3H_2$	113.6	(113.7)	113.0	(113.4)	113.5	(113.7)	113.9	(114.1)	114.4	(114.3)
$\angle M_1M_3H_3$	115.3	(114.5)	116.0	(115.1)	115.6	(115.0)	115.4	(115.0)	115.4	(115.3)
$\angle M_2M_1M_3H_2$	115.4	(114.9)	114.0	(115.1)	115.0	(115.8)	116.0	(116.5)	117.2	(117.2)
$\angle M_2M_1M_3H_3$	-119.2	(-118.4)	-120.1	(-118.6)	-119.2	(-118.2)	-118.7	(-117.8)	-117.9	(-117.6)
θ^c	115.0	(112.6)	112.6	(113.2)	113.1	(113.6)	113.6	(114.0)	114.7	(115.2)

^a Values in parentheses are at the HF/DZ level. ^b Values at the HF/3-21G (in parentheses) and HF/6-31G* levels. ^c Interflap angles between the four-membered rings.

Table 2. Strain energies and HOMO-LUMO energy levels in C_{2v} symmetry at the HF/DZ and HF/DZ+d levels.^a

	Strain energy /kcal mol ⁻¹	HOMO/eV	LUMO/eV
(1) ^b	53.8(56.5)	-10.7(-10.6)	6.1(6.8)
(2)	33.9(37.4)	-9.4(-9.4)	2.0(1.9)
(3)	29.2(32.0)	-8.8(-8.9)	1.8(1.6)
(4)	23.4(26.0)	-8.1(-8.2)	1.0(0.9)
(5) ^c	19.1(20.2)	-7.6(-7.7)	0.5(0.4)
	18.8(19.5)	-7.5(-7.4)	0.5(0.4)

^a The values in parentheses are at the HF/DZ level. ^b HF/6-31G* and HF/3-21G (in parentheses) values. ^c The second entries are for C_2 symmetry.

Table 3. Harmonic vibrational frequencies (cm⁻¹) of (5) in C_2 symmetry calculated at the HF/DZ level.

a_{symm}	13, 24, 39, 76, 104, 112, 123, 227, 243, 363, 429, 478, 494, 540, 565, 773, 777, 1805, 1826, 1829, 1837, and 1844
b_{symm}	6, 55, 87, 93, 111, 219, 231, 282, 420, 499, 523, 532, 561, 767, 775, 1802, 1825, 1828, 1832, and 1839

Table 1 summarizes the optimized geometries in C_{2v} symmetry (for atom numbering, see Figure 1). The optimized geometries of (2) and (4) agree reasonably with the *X*-ray data for the corresponding silicon and tin derivatives,^{4,5} respectively, except that the skeletons of the derivatives deviate from C_{2v} symmetry owing to the presence of bulky substituents. At the HF/DZ+d level the Pb-Pb bond distances in (5) are in the range 2.915–2.934 Å. The central Pb-Pb distance of 2.934 Å is the longest encountered but only 0.066 Å longer than the value of 2.868 Å in $H_3Pb-PbH_3$. The angles which construct the four-membered rings are almost 90°, as in (1)–(4). The interflap angle of 114.7° between the four-membered rings in (5) is rather close to the value of 115.0° in (1) and decreases slightly in the order 113.6 (4) > 113.1 (3) > 112.6° (2). As is apparent from the comparison of other geometrical parameters in Table 1, the structural features of (5) are very similar to those of (1)–(4).

Table 2 compares the strain energies calculated from the so-called homodesmotic reaction (1).¹⁰ The strain energy (53.8 kcal mol⁻¹; 1 cal = 4.184 J) of (1) at the HF/6-31G* level agrees well with the experimental estimation (51.8 kcal mol⁻¹).¹¹ In addition, the strain energy (33.9 kcal mol⁻¹) of (2) at the HF/DZ+d level is close to our previous

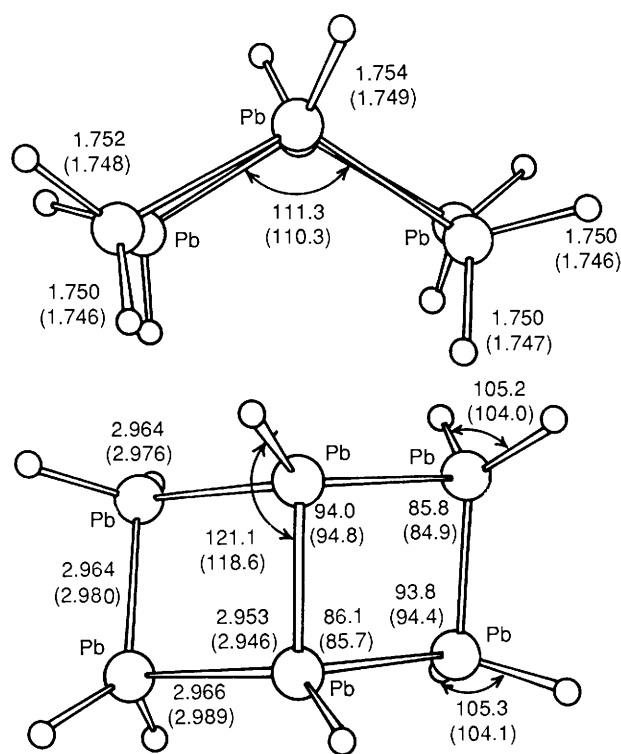


Figure 2. Two views of the C_2 optimized structures of (5) at the HF/DZ and HF/DZ+d levels. The values in parentheses are at the HF/DZ level. The total energy is -25.68002 (-25.64383) a.u.

HF/6-31G* value of 32.2 kcal mol⁻¹,¹ while the HF/DZ value of 37.4 kcal mol⁻¹ is somewhat overestimated.

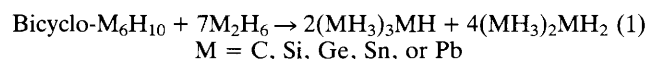


Table 2 shows that the strain energies decrease by ca. 20, 25, 30, and 35 kcal mol⁻¹, respectively, upon replacement of the C atoms in (1) by the heavier Si, Ge, Sn, and Pb atoms. Thus, the strain energy of (5) becomes as small as 19.1 kcal mol⁻¹. This results from the fact that the strain energies of four-membered C, Si, Ge, Sn, and Pb rings decrease successively in the order 26.7 (cyclobutane) > 17.2 (cyclotetrasilane) > 15.2 (cyclotetragermane) > 12.2 (cyclotetrastannane) > 10.1 kcal mol⁻¹ (cyclotetraplumbane) at the HF/DZ+d level.¹² In

fact, these values agree well with the strain energies per ring of the bicyclic compounds: 26.9 (1), 17.0 (2), 14.6 (3), 11.7 (4), and 9.6 kcal mol⁻¹ (5) at the HF/DZ+d level. The successive decrease in strain is ascribed to a stronger tendency of the heavier atoms to keep the (ns)²(np)² valence electron configuration even in compounds, release of strain producing a strong driving force for the formation of 90° bond angles in four-membered rings.

However, a vibrational frequency analysis revealed that the C_{2v} structure of (5) does not correspond to an energy minimum, unlike the cases of (1)–(4). Therefore, reoptimization was carried out without the C_{2v} symmetry constraint. As shown in Figure 2, a considerably deformed structure of C₂ symmetry was obtained which was identified as a minimum from the vibrational frequencies in Table 3. In the C₂ structure each four-membered ring is not planar but puckered, as shown by the Pb–Pb–Pb–Pb dihedral angles of 2.4 (HF/DZ) and 3.6° (HF/DZ+d), and the four angles in each ring deviate by 4–6° from 90°. Furthermore, the peripheral PbH₂ groups are rotated significantly and two hydrogens on the central Pb atoms are highly skewed from a co-planar *cis* position as characterized by the H–Pb–Pb–H dihedral angle [54.8 (HF/DZ) and 46.7° (HF/DZ+d) in C₂ vs. 0° in C_{2v}].

Despite the geometrical differences, it was calculated that the C₂ form is only 0.6 (HF/DZ) and 0.2 kcal mol⁻¹ (HF/DZ+d) more stable than the C_{2v} form. Therefore, the effect of electron correlation was incorporated on the HF/DZ+d optimized geometries with second-order Møller–Plesset perturbation (MP2) theory.¹³ However, the energy difference favouring C₂ over C_{2v} was only 0.03 kcal mol⁻¹ even at the MP2/DZ+d level,[†] suggesting that the Pb framework of (5) is remarkably flexible. This structural feature may be ascribable to the fact that Pb is most reluctant to form hybrid orbitals with high directional p character because of the (6s)² inert pair originating from the relativistic effect.¹⁴

The HOMO and LUMO energies of bicyclic compounds are also compared in Table 2. The HOMO and LUMO levels of (5) are very high and low, respectively, compared with those of (1)–(4). Thus, the energy gap between HOMO and LUMO is smallest in (5).

Compound (5) and its sterically protected derivatives form interesting synthetic targets in view of the interesting properties of the heavy polycyclic compounds.

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[†] In this context, it is interesting that in the presence of bulky substituents C₂ deformation is caused even in silicon compounds to release the steric repulsions, as seen in a derivative of (2).⁴