Found: C, 55.75; H, 6.97; N, 8.05.

Reaction of Lithium 2,3,4,5-Tetramethylpyrrolide with $[(\eta^4\text{-}C_7H_8)RuCl_2]_x$. In a three-necked round-bottom flask, equipped with a bar stirrer, nitrogen inlet, and septum, was added 2,3,4,5-tetramethylpyrrole (1.23 g, 10.0 mmol) and dry tetrahydrofuran (70 mL). To the stirred solution under nitrogen was added 6.9 mL (11.0 mmol) of a 1.6 M solution of *n*-butyllithium in hexane. The solution was stirred under nitrogen for 1 h, $[(\eta^4\text{-}C_7H_8)RuCl_2]_x$ (1.31 g 5.0 mmol) was added, and the mixture was stirred for 15 h. The solvent was evaporaed under a steady stream of dry nitrogen to give a black solid, which was extracted with two 100-mL portions of pentane. The volume of pentane was reduced under a stream of nitrogen to a volume of 5 mL and chromatographed on a 15-cm column of activity III neutral alumina. Elution with chloroform–acetone (1:1) gave a light brown solid, which was recrystallized from pentane to give 1.37 g (78% yield) of **2** as orange-brown crystals. The complex was identified as above.

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Registry No. **1**, 144467-23-2; **2**, 144467-24-3; $[Cp^*RuCl_2]_x$, 96503-27-4; $[(\eta^4\text{-}C_7H_8)RuCl_2]_x$, 42740-82-9; 2,3,4,5-tetramethylpyrrole, 1003-90-3.

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Cautions on Use of the AM1 Semiempirical Parameters for Germanium

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Summary: Caution should be exercised in the use of results employing the AM1 germanium parameters for molecules containing germanium atoms directly bonded to one another. In these cases, a smaller than expected value of the β_p parameter causes an exaggerated separation of charge. In order to demonstrate this point, a trial value of β_p was used and the results performed in the manner expected when the size of this parameter was increased. However, we *do not* recommend the replacement of the germanium β_p value. In combination with other elements, the literature values for the germanium parameters appear to perform adequately.

Introduction

In a recent AM1 investigation, we observed an unexpectedly large charge localization on germanium atoms bonded to one another. We wish to report here a more detailed analysis of the origin of this problem based on examination of the AM1 parameter values. To this end, we have examined the results of AM1 calculations on trigermapropane (germanapropane, Ge_3H_8, **1**), trigermacyclopropane (germanacyclopropane, Ge_3H_6, **2**), and tetragermacyclobutane (germanacyclobutane, Ge_4H_8, **3**).

Methodology

Semiempirical calculations were performed using the AM1[1] Hamiltonian with previously published parameter sets[2] as implemented in a slightly modified version of the AMPAC 2.1[3] computer program. A trial value for β_p on germanium was entered manually for test purposes only. Geometries were fully optimized without symmetry constraints. An examination of the matrix of second derivatives of energy with respect to atomic positions (force constants) was performed to verify that the stationary points located were minima.[4] Partial charges were calculated using the default procedure contained in the AMPAC program, which uses a Coulson analysis of the final density matrix.[5,6] In this approach, the occupancy of each atomic orbital is calculated by summing the squares of the normalized atomic orbital basis set coefficients for the occupied molecular orbitals and multiplying by the occupancy of each molecular orbital. The partial charge is then obtained by subtracting the sum of these occupancies from the number of valence electrons on each atom. Computations were carried out on the UMKC VAX 6540V from Digital Equipment Corp.

Table I. AM1 Geometries and Atomic Charges for Germanapropane (1), Germanacyclopropane (2), and Germanacyclobutane (3)

	1	2	3
Ge–Ge[a]	2.26	2.39	2.23
Ge-H	1.53	1.55	1.51, 1.54
Ge-H′[b]	1.54		
q_{Ge}[c]	+1.22	−0.10	+2.16, −2.18
$q_{Ge'}$	−1.83		
q_H	−0.20	+0.05	−0.34, + 0.35
$q_{H'}$	+0.31		

[a] Bond lengths in Å. [b] Atoms designated with a prime refer to the center GeH_2 of the propane analog. [c] Partitioned atomic charge.

Results

The AM1 geometries and charges for the germanium analogs of propane (**1**), cyclopropane (**2**), and cyclobutane (**3**) are listed in Table I. There are no experimental results available on the structure of **1**. An X-ray investigation[7] of a highly substituted analog of **2** has been published. A comparison of the Ge–Ge bond lengths obtained with AM1 and the values from experiment indicates that the AM1-calculated Ge–Ge distance is somewhat shorter than expected (2.39 vs 2.54 Å). The AM1 distance is also shorter than that predicted by ab initio calculations for unsubstituted **2** (2.50 Å).[8] AM1 also underestimates the Ge–Ge

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Table II. Atomic Orbital Electron Populations for Germanapropane (1) as a Function of β_p

	$\beta_p = -0.991091$	$\beta_p = -2.500000$
GeH$_3$ 3s	0.83	0.88
GeH$_3$ 3p	1.95	2.96
GeH$_2$ 3s	0.97	0.88
GeH$_2$ 3p	4.87	3.52

bond length in **3** in comparison to an experimental structure[9] (2.23 vs 2.46 Å) and an ab initio study employing an effective core double-ζ basis set with polarization (2.52 Å).[10]

A more serious problem becomes evident when the calculated atomic charges on the germanium atoms are compared. The cyclopropane analog (**2**) contains chemically equivalent germanium atoms. As would be predicted a priori from the modest electronegativity difference between germanium and hydrogen, the calculated charges on the germanium atoms are small. In contrast, the calculated charge separation in **1** and **3** seems to be much too large (see Table I), especially in light of the calculated charges in **2**. The localization of charge is so severe that in the case of **1** it results in the distortion of the geometry of the terminal GeH_3 groups into an almost eclipsed conformation (torsion angle ~20°), an arrangement favoring electrostatic attraction between the terminal H's (−0.20) and the central H's (+0.31). The acyclic germanapropane has two distinct atom types, and a slight difference in charge is anticipated due to chemical asymmetry, but the very substantial difference of over 3 charge units between the two types of germanium atoms falls considerably outside of the range of reasonable expectation. The cyclobutane analog (**3**) offers an example of a molecule where germaniums are bound to one another in a highly symmetric manner and all of the germanium atoms are chemically equivalent. However, AM1 computed a significant charge separation for the atoms in this molecule (+2.17, −2.16) and alternating Ge–H bond lengths (1.54, 1.50 Å).

Discussion

Examination of the AM1 germanium parameters themselves suggests a possible explanation for the strongly ionic interaction between the two types of germanium atoms in **1** and **3**. A comparison of the MNDO[10] and AM1[4] parameters for germanium shows that, for the most part, they are very similar. The notable exception is β_p,[11] one of the parameters used in determining the value of the resonance integral between the p orbitals of germanium and the orbitals on other atoms. This value is almost 50% *smaller* in AM1 than in MNDO (AM1 = −0.991 091, MNDO = −1.755 517). This significantly reduces the interaction of p electrons on Ge atoms with the orbitals of other atoms, resulting in charge separation. The effects of this phenomenon will become most pronounced in compounds containing Ge–Ge bonds.[12]

In order to test our conclusions about the role of β_p in this connection, a second calculation on **1** was performed using a trial value for β_p of −2.500 000.[13] The charges from this calculation ($q_{Ge} = +0.16$ and $q_{Ge'} = -0.40$) are much smaller than before, which is the expected trend when there is greater interaction of germanium p orbitals with the orbitals on other atoms. Further, examination of the resultant wave functions showed a definite difference when the larger value of β_p was used. The coefficients of the p atomic orbitals indicated that they contribute to the molecular orbitals in a much more even fashion when the larger β_p value is utilized. This is dramatically illustrated by examining the atomic orbital electron populations (see Table II).[14] The larger value of β_p results in a relatively uniform occupancy of the p orbitals on the two types of germanium atoms, consistent with the lower charges. Thus, the trial β_p value gives a description more in line with the traditional four-bond/sp^3 covalent bonding pattern expected for a tetracoordinated atomic center.

Examining the results obtained for the cyclic and acyclic germanium analogs of propane, it is reasonable to assume that the difference in charge is due to molecular asymmetry, i.e. nonequivalent germanium atoms. However, results in the case of **3** show that this explanation is oversimplified. The apparent cause of charge separation is the ability of some wave functions to become asymmetric, allowing uneven contribution by the p orbitals on different atoms to the molecular orbital manifold. This occurs even in cases where atoms should be chemically equivalent. Comparison of the molecular orbitals for cyclobutane and **3** indicates that the degeneracy of orbitals having E_u and E_g symmetry[15] in cyclobutane is removed in the case of the germanium analog.

Given the small value of β_p and the effects noted above, it is reasonable to wonder how an adequate description of any molecule containing germanium can be obtained using the AM1 parameters. In an attempt to explain this, we undertook a careful examination of all of the available AM1 parameters. The results of this examination show that Ge is the only case in which the Slater exponent[16] for the valence s orbital (ζ_s) indicates *less contraction* than the exponent for the p orbital (ζ_p).[17] Note that the resonance integral ($\beta_{\mu\lambda}$) is calculated[8] within the NDDO approximation using

$$\beta_{\mu\lambda} = \frac{\beta_\mu{}^A + \beta_\lambda{}^B}{2} S_{\mu\lambda}$$

where β_μ and β_λ are atomic parameters for the s and/or p orbitals on atoms A and B, respectively, and $S_{\mu\lambda}$ is the overlap integral matrix element between orbitals $\phi_\mu{}^A$ and $\phi_\lambda{}^B$. Apparently, the parameterization procedure compensated for the small value of β_p for germanium by increasing the size of germanium's s orbital ($\zeta_s < \zeta_p$, implying s is *larger* than p). This has the effect of increasing overlap and therefore compensates to some extent for the reduced bonding contribution by p orbitals. It should also be pointed out that since the β values of both atoms in a bond are used to approximate the resonance integral, the small magnitude of germanium's β_p contribution is mitigated by averaging it with β from the other atom. The worst situ-

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[10] Dewar, M. J. S.; Grady, G. L.; Healy, E. F. *Organometallics* **1987**, *6*, 186.

[11] For discussion of the MNDO/AM1 parameter scheme see: Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4907.

[12] It should be ntoed that no molecules possessing asymmetrically disposed germaniums bonded to one another were present in the original molecular parameterization set or in the molecular test set; thus, this phenomenon would not have been observed in the development and testing of these parameters.

[13] This value for β_p is extrapolated from the AM1 parameter values for other elements on the third row of the periodic table.

[14] The population of atomic orbital ϕ is defined as

$$\text{Pop.}(\phi) = \sum_{i=1}^{\text{MO}} n c_{i\phi}{}^2$$

where n is the number of electrons occupying the MO.

[15] Symmetry labels assume idealized, planar molecules having D_{4h} symmetry.

[16] The form of the Slater orbitals is

$$\phi = f(r)\, e^{-\zeta r}$$

[17] For AM1 germanium, $\zeta_s = 1.293180$ and $\zeta_p = 2.020564$.

ation occurs when two germaniums are directly bonded. In this case, extreme charge separation due to the small resonance integral becomes allowed.

This set of AM1 parameters illustrates a danger inherent to the flexibility of the semiempirical approach to quantum mechanics. Care must be taken in deriving parameters for the methods. Chemical knowledge and reasoned guidance are needed to develop parameters of chemical significance. The "human factor" is of paramount importance, as the best *mathematical* minima on the parameter hypersurface may not be the best *chemical* minima.[18]

In conclusion, caution should be exercised in calculations employing the AM1 germanium parameters when germanium atoms are bonded to one another. In this case, the tendency to localize charge is greatest. In combination with other elements, the germanium parameters appear to perform adequately. We *do not* recommend the replacement of the germanium β_p value. This would require a complete reparameterization for germanium, as the atomic parameters for an element are strongly interdependent (see above). It must be emphasized that setting $\beta_p = -2.500000$ was used for *trial* calculations, intended to illustrate that the magnitude of the AM1 value was too small.[19] It is NOT PROPOSED as a replacement for the default parameter. We in no way intend to encourage the manual alteration of parameters to achieve particular effects.

With elucidation of the current problem with the germanium parameters for AM1, it is apparent that this element should be reparameterized. With most elements, this is not an option because the developed values are used in subsequent parameterizations of other elements. This is not the case with germanium. Germanium data have not been used in any other molecular basis set for parameterization. While uncommon, silicon[20] and sulfur[21] were also reparameterized within the MNDO protocol due to poor performance. We do not wish to call for a general reparameterization, but in this single instance new work seems justified.

Registry No. Ge, 7440-56-4.

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[18] Parameterization schemes used for semiempirical methods generally rely on comparison of calculated values with a limited set of experimental data. Obviously, any such parameterization scheme is biased by the experimental data available or by the specific subset of molecules chosen for the basis set.

[19] The β_p value was altered to examine a specific feature of the performance of the germanium parameters and caused a number of other difficulties which were not listed. As an example, the heat of formation of 1 became over 165 kcal/mol more stable than the original parameters predicted.

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Electrophilic Thallation of Thiophene Derivatives and Furan with Phenylthallium(III) 18-Crown-6 Diperchlorate

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Summary: Electrophilic thallation of thiophene and its derivatives (2-methyl-, 2-chloro-, 2-bromo-, and 2-iodothiophenes, 2-thiopheneacetonitrile, 2-thiophenecarbonitrile, 3-methyl- and 3-bromothiophenes, and 3-thiophenecarboxaldehyde) as well as furan using (18-crown-6)phenylthallium(III) diperchlorate (**1**) (**1** is also named as phenylthallium(III) 18-crown-6 diperchlorate) was studied. The thallation occurred at the position α to the sulfur atom of thiophene and the oxygen atom of furan, affording the corresponding (18-crown-6)phenylarylthallium(III) perchlorate complexes **2**–**12**. The thallations of thiophenecarboxaldehydes took place without oxidation of the aldehyde groups.

In contrast to well-known aromatic thallation by inorganic Tl^{III} species, TlX_3, examples of electrophilic thallation by organothallium(III) compounds, e.g. $ArTlX_2$, have been limited.[1] The latter is interesting and important since it affords a mixed diarylthallium(III) compound that is a member of a relatively unknown class of organothallium compounds. Recently we have reported that a phenylthallium(III) complex having a crown ether, $[PhTl^{III}(18\text{-crown-}6)](ClO_4)_2$ (**1**), can initiate electrophilic thallation of phenols,[2] aromatic amines,[3] and pyrroles.[3] The presence of the crown ether is essential for a clean

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