N′,N″-triphenylisocyanurate,[45] and IR spectra of the crude reaction mixture, which indicated complete consumption of the initial 4 equiv of PhNCO, also exhibited a moderately strong absorption at 1712 cm^{-1} which suggested formation of significant quantities of the cyclic trimer.

Competitive cyclotrimerization was an even more significant problem with the group 8 metals, and there was no observable reduction of CH_3NO or PhNCO by Collman's reagent. Addition of either heteroallene (6 equiv) to a THF suspension of Collman's reagent at 25 °C led exclusively to cyclotrimerization,[45,46] suggesting that cyclotrimerization, which is base catalyzed, is faster under these conditions than addition to $[Fe(CO)_4]^{2-}$.

Reactions of Carbodiimides with Collman's Reagent. The reduction of carbodiimides potentially provides an alternative approach to monoisonitrile complexes, but experiments with Collman's reagent suggested that this was not, in practice, a useful reaction. Although the reaction of $Na_2[Fe(CO)_4]\cdot 1.5$*p*-dioxane with PhNCNPh did lead to the formation of $[Fe(CO)_4(CNPh)]$, the isolated yield was small (10%), and, since similar experiments with the cyclohexyl analogue $C_6H_{11}NCNC_6H_{11}$ did not lead to detectable levels of $[Fe(CO)_4(CNC_6H_{11})]$ after 6.5 h at 25 °C, no further experiments were conducted with carbodiimides.

Conclusions

The results above establish that dianionic carbonylmetalates of the group 6 and group 8 metals can reduce a number of heteroallenes X=C=Y other than CO_2 to coordinated C≡X ligands, provided X is a first-row element (N or O) which can form a strong triple bond with C. We have, for example, seen no cases of formation of a coordinated thiocarbonyl, and the marked preference for the formation of carbonyl ligands rather than isonitriles (as shown by the reaction of $Na_2[W(CO)_5]$ with PhNCO and by the higher yields of carbonyl complexes from reactions with COS than of isonitriles from reduction of thioisocyanates) is consistent with control of the direction of reduction of asymmetric heteroallenes by the relative strengths of the C≡X bands formed. The failure to observe reductive disproportionation of CS_2 suggests that the strength of the C=X bond being cleaved is not an important factor, since the C=S bond is weaker than the C=N and C=O bonds, but in the absence of detailed thermochemical data we cannot rule out the possibility that the strength of the M—C bonds being formed is also important.

Acknowledgment. This work was supported in part by the Office of Naval Research.

Registry No. COS, 463-58-1; PhNCS, 103-72-0; MeNCS, 556-61-6; PhNCO, 103-71-9; PhNCHPh, 622-16-2; $Na_2[Fe(CO)_4]$, 14878-31-0; $Na_2[Ru(CO)_4]$, 57398-60-4; $Na_2[Cr(CO)_5]$, 52154-81-1; $Na_2[W(CO)_5]$, 54099-82-0; $Li_2[Cr(CO)_5]$, 109283-12-7; $[Fe(CO)_5]$, 13463-40-6; *cis*-$[Fe(CO)_4I_2]$, 14911-55-8; $[Ru(CO)_5]$, 16406-48-7; *cis*-$[Ru(CO)_4I_2]$, 18475-75-7; $[Cr(CO)_6]$, 13007-92-6; [N(*n*-Bu)$_4$]$[Cr(CO)_5Br]$, 78022-78-3; $[W(CO)_6]$, 14040-11-0; [N(*n*-Bu)$_4$]$[W(CO)_5Br]$, 67846-99-5; $[Fe(CO)_4(CNPh)]$, 17595-21-0; $[Fe(CO)_4(CNCH_3)]$, 14741-64-1; $[Cr(CO)_5(CNPh)]$, 14782-94-6; $[W(CO)_5(CNPh)]$, 15612-93-8; $Na[Cr(CO)_5SC(O)H]$, 120311-05-9; $Na[W(CO)_5SC(O)H]$, 120311-06-0; ClCOCOCl, 79-37-8.

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(45) Kogon, I. C. *J. Am. Chem. Soc.* **1956**, *78*, 4911.

(46) For a report on cyclotrimerization of CH_3NCO see: Fukui, K.; Tanimoto, F.; Kitano, H. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 1586.

AM1 Calculations for Compounds Containing Germanium

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AM1 has been parametrized for germanium. Calculations are reported for a number of compounds of germanium. The results are generally superior to those from MNDO, especially in geometries.

Introduction

Now that germanium is readily available as a result of its importance in electronics, increasing attention is being paid to its chemistry.[1] As a result, there is a growing need for a practical theoretical procedure for studying the behavior of germanium compounds. While ab initio methods are of limited value for studies of elements from the third and later rows of the periodic table, MNDO[2] and AM1[3] have proved effective in this connection. AM1, the most recent of our semiempirical procedures, has been parametrized successfully for the halogens,[4] silicon,[5] zinc,[6] mercury,[7] and phosphorus,[8] as well as boron[9] and the "organic" elements,[3] while MNDO has also been parametrized for all the main group IV elements, including germanium.[10] The errors in the MNDO heats of formation for germanium compounds were, however, larger than usual. Since AM1 has proved generally superior to MNDO, there is clearly a need for it to be extended to germanium. Here we report AM1 parameters for it.

Table I. Optimized AM1 Parameters for Germanium

optimized parameters	AM1	MNDO
U_{ss}, eV	−34.183 889	−33.949 367
U_{pp}, eV	−28.640 811	−27.425 105
ζ_s, au	1.219 631	1.293 180
ζ_p, au	1.982 794	2.020 564
β_s, eV	−4.356 607	−4.516 479
β_p, eV	−0.991 091	−1.755 517
a, Å^{-1}	2.136 405	1.978 498
G_{ss}	10.168 605	9.800 000
G_{pp}	6.671 902	7.300 000
G_{sp}	8.144 473	8.300 000
G_{p2}	6.269 706	6.500 000
H_{sp}	0.937 093	1.300 000

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(1) (a) Riviere, P.; Riviere-Baudet, M.; Satge, J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergamon: New York, 1982; Vol. 2. (b) Lesbre, M.; Mazerolles, P.; Satge, J. *The Organic Compounds of Germanium*; Wiley: New York, 1972.

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Table II. Calculated Heats of Formation (kcal/mol), Ionization Potentials (eV), and Dipole Moments (D) for Molecules Containing Germanium[a]

	ΔH_f			dipole			IP		
compd	AM1	obsd	error	AM1	obsd	error	AM1	obsd	error
Ge_2	128.6	113.0[b]	17.6				8.33		
GeO	9.2	-11.0[b]	20.2	2.62	3.28[c]	-0.66	9.40		
GeF	-19.7	-8.0	-11.7	0.04			7.21		
GeCl	19.6	37.0	-17.4	0.79			7.72		
GeBr	43.2	56.3	-13.1	0.30			8.16		
GeC	203.6	151.0[b]	52.6	0.32			10.39		
GeF_2	-123.4	-121.0	-2.4	1.27	2.61	-1.34	9.25		
$GeCl_2$	-42.9	-42.0	-0.9	1.32			9.49		
$GeBr_2$	1.0	-15.0	16.0	0.00			9.40		
GeI_2	43.4	11.2[b]	32.2	0.00			9.54		
GeH_4	29.0	21.7[b]	7.3				11.49	11.31	0.18
GeH_4^+	289.8	284.1[b]	5.7				18.59		
$GeMe_3$	-1.7	2.2	-3.9	0.04			8.46	8.00	0.46
GeF_4	-263.3	-284.4	21.0				14.58		
$GeCl_4$	-138.7	-118.5	-20.2				13.02	11.88	1.15
$GeCl_4^+$	160.1	156.8[b]	3.3				18.64		
$GeBr_4$	-69.5	-71.7	2.2				11.92		
GeI_4	3.7	-13.6	17.3				11.33		
$Ge(CH_3)_4$	-26.4	-32.0	5.6				10.97	9.29	1.68
$(CH_3)_3GeCl$	-58.6	-63.8	5.2	2.56	2.78	-0.22	11.17	10.50	0.67
$(CH_3)_3GeBr$	-41.0	-53.1	12.1	2.59	2.84	-0.25	10.69	10.00	0.69
$Ge(CH_3)_3(t\text{-}Bu)$	-45.7	-55.7	10.0	0.16			9.91	8.98	0.93
$Ge(CH_3)NMe_2$	-27.7	-29.1	1.4	0.25			8.69		
$(CH_3)_3GeOC_2H_5$	-90.2	-87.8	-2.4	1.53			10.33		
$Ge(C_2H_5)_4$	-60.0	-39.7	-20.3				10.28		
$Ge(OCH_3)_4$	-252.5	-230.4	-22.1				10.99		
$((CH_3)_3Ge)_2O$	-111.7	-127.0	15.3	1.52	1.41	0.11	10.43		
$Ge_2(CH_3)_6$	-41.2	-62.5	21.3				9.96	8.18	1.78
Ge_2H_6	39.1	38.8	0.3				10.03		
Ge_3H_8	41.8	54.2	-12.4	0.66			10.38		
$Ge(CH_3)_3^+$	180.5	165.0	15.5				17.05		
$Ge(CH_3)_3$	-1.3	2.2	-4.5	0.04			8.21	8.00	0.21
GeH_3I	23.1			1.65	1.81[c]	-0.16	10.56		
$(CH_3)GeCl_3$	-114.9			2.54	2.70[c]	-0.16	11.97		
$(CH_3)GeN$	110.5			2.20	3.99[c]	-1.79	10.89		
$(CH_3)GeH_3$	15.2			0.14	0.64[c]	-0.50	11.05		
$(C_2H_3)GeBr_3$	-19.9			2.80	2.47[c]	0.33	11.05		
$(CH_3)_2GeCl_2$	-88.1			2.91	3.14[c]	-0.23	11.48		
$(CH_3)_2GeH_2$	1.4			0.09	0.62[c]	-0.53	10.98		
$(CH_3)_3GeH$	-12.5			0.05	0.67[c]	-0.62	10.94		
$(CH_3)_3Ge(OCH)_3$	-84.6			1.64	1.73[c]	-0.09	10.47		
$(CH_3)_2Ge(OCH_3)_2$	-142.8			2.19	1.63[c]	0.56	10.52		
$CH_3Ge(OCH_3)_3$	-199.8			1.18	1.91[c]	-0.73	10.81		

[a] Except where noted, for references of experimental values, see: Dewar, M. J. S.; Grady, G. L.; Healy, E. F. *Organometallics* **1987**, *6*, 186. [b] Wagman, D. D., et al. *J. Phys. Chem. Ref. Data*, **1982**, *11*, Suppl. 2. [c] McClellan, A. L. *Tables of Experimental Dipole Moments*; Rahara Enterprises: el Cerrito, CA, 1974.

It was assumed in the past that differences in behavior between first-row elements, and later row elements, were due to the lack of d AOs in the valence shells of the former. If this were true, it would invalidate the use of MNDO and AM1 for other than first-row elements because neither incorporates d AOs. However, it now seems clear[11-14] that the traditional view is incorrect, at least for main-group elements in their normal valence states. The differences are due to the greater size of atoms of later period elements, d AOs playing at most a secondary role. Indeed, we have recently succeeded in obtaining a set of AM1 parameters which reproduces the behavior of compounds of phosphorus in both its valence states.[8] Any contributions by phosphorus d AOs must be far greater for P^V than for P^{III}.

Procedure

The AM1 parameters for germanium were determined by a least-squares fit to selected properties of a selected set (basis set) of molecules, using standard AM1 parameters[3,4] for the other elements. The parametrization procedure involves the minimization of an error function (SSQ), defined as a sum of the squares of the differences between the individual calculated and experimental values, suitably weighted for different properties. The choice of molecules in the basis set, and the values of the weighting factors, are found by trial and error, on the basis of chemical acceptability of the final results. The development of effective procedures of this kind thus depends on chemical judgement.

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(2) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899, 4907.
(3) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.
(4) Dewar, M. J. S.; Zoebisch, E. G. *THEOCHEM* **1988**, *180*, 1.
(5) Dewar, M. J. S.; Jie, C. X. *Organometallics* **1987**, *6*, 1486.
(6) Dewar, M. J. S.; Merz, K. M., Jr. *Organometallics* **1988**, *7*, 522.
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(9) Dewar, M. J. S.; Jie, C. X.; Zoebisch, E. G. *Organometallics* **1988**, *7*, 513.
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(14) Dewar, M. J. S.; Storch, D. M., to be submitted for publication.

Table III. Calculated and Observed Geometrical Parameters[a]

molecule	point group	geometries[a] calcd (obsd)				ref[a]
GeO	$C_{\infty v}$	GeO	1.624 (1.625)			
GeH_4	T_d	GeH	1.546 (1.527)			
Ge_2H_6	D_{3d}	GeGe	2.370 (2.403), GeH	1.549, HGeGe	110.5	*b*
GeF_2	C_{2v}	GeF	1.673 (1.732), FGeF	94.2 (97.2)		
$GeClF_3$	C_{3v}	GeF	1.703 (1.688), GeCl	2.171 (2.067), FGeCl	113.2 (111.4)	
$GeFH_3$	C_{3v}	GeF	1.716 (1.730), GeH	1.540 (1.522), FGeH	105.5 (105.66)	
$GeBrH_3$	C_{3v}	GeBr	2.256 (2.297), GeH	1.553 (1.535), BrGeH	109.4 (109.9)	
CH_3GeH_2F	C_s	GeF	1.714 (1.751), GeC	1.970 (1.925), CGeF	107.0 (106.3)	
$GeCN(CH_3)_3$	C_3	GeC(N)	1.899 (1.947), GeC	1.963 (1.930), CGeC(N)	109.7 (106.2)	
$GeH_3C_2H_3$	C_s	GeC	1.943 (1.926), GeH	1.542 (1.520), CGeH	108.0 (109.7)	
		CCGe	125.5 (122.9)			
$GeCNH_3$	C_{3v}	GeC	1.887 (1.919), GeH	1.539 (1.525), CGeH	108.8	
$GeH_3C_2H_5$	C_s	GeC	2.004 (1.949), GeH	1.545 (1.522), CGeH	107.3 (109.7)	
GeH_3CH_3	C_{3v}	GeC	1.988 (1.945), GeH	1.545 (1.534), CGeH	107.3 (110.3)	
$GeHCl_3$	C_{3v}	GeH	1.559 (1.550), GeCl	2.131 (2.114), ClGeH	111.6 (108.3)	
$GeH(CH_3)_3$	C_3	GeH	1.543 (1.522), GeC	1.982 (1.947), CGeH	110.9 (109.3)	
$GeCl(CH_3)_3$	C_3	GeCl	2.152 (2.170), GeC	1.977 (1.940), CGeCl	108.0 (105.9)	
$GeBr(CH_3)_3$	C_3	GeBr	2.280 (2.323), GeC	1.988 (1.936), CGeBr	110.3 (106.3)	
$GeIH_3$	C_{3v}	GeI	2.433 (2.508), GeH	1.554, IGeH	110.6	
GeF_4	T_d	GeF	1.706 (1.73)			*c*
$GeCl_4$	T_d	GeCl	2.148 (2.113)			*d*
$Ge(CH_3)_4$	C_3	GeC	1.981 (1.945), CH	1.107 (1.12)		*d*
H_3CGeCl_3	C_{3v}	GeCl	2.136 (2.135), GeC	1.988, CGeCl	110.2 (106.0)	
H_3GeSiH_3	C_{3v}	GeSi	2.215 (2.357), GeH	1.544, HGeSi	109.2	
$Ge_2O(CH_3)_6$	C_s	GeC	1.971 (1.980), GeO	1.850 (1.770), GeOGe	120.9(141)	
		GeOC	106.3 (109)			*e*

[a] Bond lengths in Å; angles in deg. For references, except where noted, see: Harmony, M. D.; Laurie, V. W.; Kuczkowski, R. L.; Schwendeman, R. H.; Ramsay, D. A., et al. *J. Phys. Chem. Ref. Data* **1979**, *8*(3), 619. [b–d] Moreno, Y.; Nakamura, Y.; Iijima, T. *Can. J. Chem. Phys.* **1960**, *32*, 643. [e] Hencher, J. L.; Mistoe, F. J. *Can. J. Chem.* **1975**, *53*, 3542. [f] Vilkov, L. V.; Tarensenko, N. A. *Zh. Strukt. Khim.* **1969**, 10, 102.

The experimental values used in the parameterization included heats of formation, ionization potentials, dipole moments, and geometries. The minimization of SSQ uses a derivative optimization,[15] based on the Davidon–Fletcher–Powell (DFP) algorithm.[16] The first derivatives of the heats of formation and ionization energies with respect to the parameters were calculated analytically, while derivatives of the dipole moment and geometries were found by finite differences. The derivatives of the energy at the experimental geometry served as a measure of the deviation of the calculated geometry from experiment.

The calculations were carried out by using the standard AM1 procedure and parameters, as implemented in the AMPAC package of computer programs.[17] The only quantities in AM1 that depend on the period to which an atom belongs are the relevant overlap integrals. AMPAC provides for their calculation for all elements.

Results and Discussion

Table I shows the final values for the parameters in the notation used previously.[2,17] Most of them differ little from the corresponding MNDO parameters. The only large difference is for B_p, the AM1 value being more negative.

AM1 differs from MNDO primarily by the inclusion of additional Gaussian terms in the core repulsion function. Here Gaussians were not included because the lack of experimental data, in particular thermochemical data, made it necessary to keep the number of parameters to a minimum. We reoptimized the one-center, two-electron parameters (g and h) from their previous values.[10] Since different s and p values were used for ζ and β, the total number of parameters for germanium is the same in AM1 as it was in MNDO.

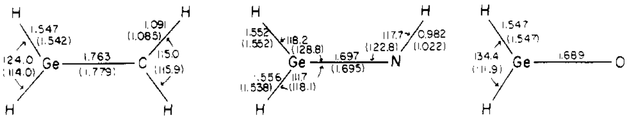

Figure 1. AM1 optimized geometries for the lowest singlet states of germaethylene, germanimine, and germanone. Ab initio results are shown in parentheses; see ref 17.

Table II lists the heats of formation (ΔH_f), dipole moments (μ), and first ionization potentials (IP), calculated for molecules containing germanium, together with available experimental values for comparison. The IPs were estimated from orbital energies, using Koopmans' theorem. MNDO values are also included.

The mean absolute error in ΔH_f for 31 germanium-containing molecules (13.1 kcal/mol) represents a very significant improvement over MNDO (19.5 kcal/mol). The results are satisfactory, especially since the accuracy of many of the experimental values is uncertain. Furthermore, two rather exotic molecules account for a large part of the error (GeC, 52.6 kcal/mol; GeI, 32.2 kcal/mol). In the case of MNDO, there were large positive errors in the heats of formation calculated for compounds containing more electronegative atoms. This problem has been overcome in AM1.

The mean absolute error in the dipole moments of 16 molecules is 0.51 D (Table II). Here again a significant part of the AM1 error is due to large contributions by two molecules (CH_3GeN; 1.79 D; GeF_2, −1.34 D). The average MNDO error, for three molecules, was 0.45 D.

The calculated IPs are systematically too large. However, the mean absolute error for the nine molecules in Table II (0.91 eV) is less than the corresponding error (1.32 eV) in MNDO. Similar errors occur generally in IPs calculated by MNDO or AM1 for compounds containing

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(15) See: (a) Dewar, M. J. S.; Grady, G. L.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1984**, *106*, 6771. (b) Dewar, M. J. S.; Grady, G. L.; Kuhn, D. R.; Merz, K. M., Jr. *Ibid.* **1984**, *106*, 6773.

(16) Davidon, W. C. *Comput. J.* **1958**, *1*, 406. Fletcher, R.; Powell, M. J. D. *Ibid.* **1963**, *6*, 163.

(17) Available from QCPE, Department of Chemistry, Indiana University, Bloomington, IN 47405.

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Table IV. Average Errors in Geometries of Some Bond Lengths and Angles

type of bond	no. of compds	AM1
Ge–H[a]	9	0.017
Ge–C	12	0.037
Ge–O	2	0.040
Ge–F	5	0.030
Ge–Cl	5	0.035
Ge–Br	2	0.042
CGeH	4	2.2
CGeCl	2	3.1

[a] All calculated bond lengths have positive errors (longer than the observed values).

later row elements. They have been attributed to the neglect of interactions between the inner-shell and valence-shell electrons, due to use of the core approximation in MNDO and AM1.

Table III compares the calculated geometries with experiment while Table IV analyses the average errors in the lengths of various kinds of bonds. The mean error for Ge–H bond lengths is much less in AM1 than MNDO. Since germanium forms long bonds, the average errors listed in Table IV are all small in percentage terms.

Figure 1 shows the AM1 geometries of some germanium compounds containing germanium double bonds. While no experimental values are available for comparison, results from a recent high level pseudopotential calculation are included (in parentheses) in Figure 1, for comparison. While both methods predict similar bond lengths, AM1 gives a larger H–Ge–H bond angle.

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AM1 Calculations for Compounds Containing Mercury

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AM1 has been parametrized for mercury. Calculations are reported for a number of mercury-containing compounds. The results are generally better than those given by MNDO.

Introduction

While the MNDO[1] and AM1[2] semiempirical SCF MO methods cannot be applied to transition metals because of the omission of d AOs, MNDO has been successfully extended to several main-group metals (lithium,[3] beryllium,[4] aluminum,[5] zinc,[6] tin,[7] lead,[8] and mercury[9]). Since AM1 has proved generally superior to MNDO, we are currently extending it to the "MNDO" elements. Here we report AM1 parameters for mercury.

Procedure

The AM1 parameters for mercury were determined by a least-squares fit of the calculated (AM1) values of various properties of a selected set (basis set) of molecules to experiment, using a recently described[7] optimization procedure. This involves the minimization of an error function (SSQ) defined as a sum of the squares of the differences between the individual calculated and experimental values, suitably weighted for different properties. The best values for the weighting factors are found by trial-and-error, on the basis of the chemical acceptability of the final results. The minimization is carried out by a recently described procedure,[7] based on the Davidon–Fletcher–Powell (DFP) algorithm.[10] The first derivatives of the heats of formation and ionization energies with respect to the various parameters are calculated analytically. The derivative of the energy with respect to each geometrical variable is taken as a measure of the error in the latter.

The properties used in the parametrization included heats of formation, ionization energies, dipole moments, and geometries. The calculations were carried out by using the standard AM1 procedure and parameters, as implemented in the AMPAC program.[11] The only quantities

Table I. Optimized AM1 Parameters for Mercury

optimized parameters	value	MNDO
U_{ss}, eV	−19.941 578	−19.809 574
U_{pp}, eV	−11.110 870	−13.102 530
ζ_s, au	2.036 413	2.218 184
ζ_p, au	1.955 766	2.065 038
β_s, eV	−0.908 657	−0.404 525
β_p, eV	−4.909 384	−6.206 683
α, Å^{-1}	1.484 734	1.335 641
G_{ss}	10.800 000	
G_{pp}	14.300 000	
G_{sp}	9.300 000	
G_{p2}	13.500 000	
H_{sp}	1.300 000	

[†] On leave of absence from Lanzhou University, Lanzhou, The People's Republic of China.

(1) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899, 4907.

(2) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(3) While parameters for lithium were developed some years ago by Professor W. Thiel and have been used with success in numerous studies of lithium compounds, notably by Professor Schleyer's group at Erlangen, they have never been formally published. They are, however, included in the MOPAC and AMPAC programs.

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