

Optimization and Application of Lithium Parameters for PM3

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Lithium parameters have been optimized for Stewart's standard PM3 method. The average deviation of the heats of formation calculated for 18 reference compounds is 6.2 kcal/mol from the experimental or high-level *ab initio* data; the average deviation with Li/MNDO is 18.9 kcal/mol. The average error in bond lengths is also reduced by a factor of two to three. Ionization potentials and dipole moments are reproduced with comparable accuracy than Li/MNDO. However, the mean deviation for the heats of formation of both methods increases when being applied to other systems, especially to small inorganic molecules. The applicability of the new parameter set is demonstrated further for various compounds not included in the reference set, for the calculation of the activation barriers of several lithiation reactions, as well as for the estimation of oligomerization energies of methyl lithium (including the tetramer). Li/PM3 gives reliable results even for large dimeric complexes, like $[\{4-(\text{CH}_3\text{CR})\text{C}_5\text{H}_4\text{N}\}\text{Li}]_2$, containing TMEDA or THF as coligands and reproduces the haptotropic interaction between Li^+ and π -systems (e.g., in benzyl lithium) as well as the relative energies and structural features of compounds with "hypervalent" atoms (e.g., in lithiated sulfones). © 1993 by John Wiley & Sons, Inc.

INTRODUCTION

Organolithium compounds, increasingly important reactive intermediates,^{1,2} are frequently the reagents of choice for a variety of synthetic purposes because they are often more useful than other alkali metal and magnesium compounds. However, lithium reagents are complex and methods to obtain more reliable information are needed. MO calculations provide a detailed insight into lithium-containing molecules. Such studies allow a comprehensive survey of both structural and energetic information based on well-defined levels of theory. Reliable experimental data of lithium compounds [especially heats of formation, dipole moments, and ionization potentials (IPs)] are rare. The application of high-level *ab initio* methods exceeds the present computer capacity of most research groups: realistic structure-reactivity patterns of this class of compounds can only be reproduced by aggregated and solvated molecules. Therefore, the application of the (three popular) semiempirical MO methods, i.e., MNDO,³ AM1,⁴ and PM3,^{5,6} is clearly desirable because of their ability to calculate large molecules, albeit with a certain degree of inaccuracy. Unfortunately, only one of these methods, MNDO, has

been extended to lithium.^{7*} For almost 15 years, this parameterization has been the only one available for the so-called "Dewar" semiempirical methods, although SINDO/1^{8,9} is also suitable for calculating organolithium structures and energies. One reason is the dearth of reliable and sufficiently broad reference thermochemical and structural experimental data. Such a set should at least include Li-C, Li-N, and Li-O interactions featuring single, double, or triple bonds. Because organolithium compounds are reactive, only a few gas-phase measurements are available.

In the past decade, Li/MNDO has been applied successfully to many problems^{2,10,11} and is useful for obtaining properties of lithium compounds. However, the Li/MNDO parameter set from its inception was known to have some severe deficiencies, e.g., the overestimation of the C-Li and H-Li interaction.¹²

Reliable reference data¹³ for organolithium compounds from high-level *ab initio* calculations,¹⁴⁻¹⁷ combined with the rare experimental data (also for inorganic lithium compounds^{18,19}), provided a sufficiently flexible data base for the parameterization.

This article is dedicated to Prof. Dr. A.R. Katritzky on the occasion of his 65th birthday.

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*This work has never been published in full. None of the five parameter sets originally derived were entirely satisfactory. The one chosen for use had known deficiencies that have been mentioned many times in the literature—the C-Li and H-Li interactions are overestimated.

METHOD

PM3 appears to be the best choice for a new lithium parameterization. While AM1 overcomes many of the major deficiencies of MNDO,²⁰ e.g., the overestimation of interaction energies in sterically crowded molecules and the underestimation of strain energy in four-membered rings and the failure to reproduce hydrogen bonding correctly, some problems remain, e.g., the lone-pair/lone-pair repulsion in various heterocyclic compounds and in *Z*- and *E*-diazene is underestimated by AM1.²¹ PM3 allows a better description of this repulsion. The calculation of hypervalent molecules was improved and the average error in heats of formation was further reduced. Nevertheless, this method cannot be regarded as generally superior to AM1.²²⁻²⁵

The treatment of the one-center two-electron repulsion integrals is the major difference between AM1 and PM3. AM1, like MNDO, uses the fixed values of Oleari.²⁶ In PM3, in contrast, all parameters are treated as variables. This larger number of optimizable parameters leads to greater flexibility and a higher probability of "suitable" parameters at the cost of extra computation time for the parameterization.

As pointed out by Stewart, parameters for all elements available should in principle be optimized simultaneously, even when the method is extended to only one new element.²⁷ However, to prevent changes in widely used standard parameters (which do not lead to significant improvement) only the parameters for lithium were optimized, while all others were held constant.

The general procedure used here to obtain optimized parameters is based on Stewart's standard method for PM3.²⁸ After setting up a data base, all available reference functions, i.e., heats of formation, geometry parameters, dipole moments, and ionization potentials, were transformed into dimensionless quantities by multiplication with a weighting factor. The same procedure was applied to the calculated properties, which were derived from full geometry optimizations. With these two dimensionless numbers, q_i^{calc} and q_i^{exp} , an error function S can be determined: $S = \sum (q_i^{\text{calc}} - q_i^{\text{exp}})^2$. The weighting factors used in this procedure are 1 mol · kcal⁻¹ for heats of formation, 100 Å⁻¹ for bond lengths, 10 D⁻¹ for dipole moments, and 10^{eV}⁻¹ for ionization potentials. Minimization of the error function S leads at least to a local minimum. The aim, however, is to find the global minimum. Unfortunately, this procedure does not include a well-defined search criterion for the global minimum. Therefore, testing the parameter set obtained (Table I) with a wide variety of molecules is an important and substantial part of this article. After extensive checking, it seems unlikely that a significantly "better" parameter set could exist. Some of these, in our opinion, representative

tests are summarized below and in Tables VI–XI. The reference molecule data are collected in Tables II–V.

RESULTS

Properties for a variety of compounds calculated with the newly developed PM3 parameters are compared (together with those obtained with Li/MNDO) with experimental and high-level *ab initio* data. Further, the potential applicability of Li/PM3 to heats of formation, geometries, dipole moments, ionization potentials, oligomerization and activation energies, transition states, and the structural properties of dimeric TMEDA and THF complexes is surveyed. All semiempirical calculations were performed on IBM-compatible personal computers using MOPAC6/PC.²⁹ Gaussian 90³⁰ was employed for the *ab initio* calculations using the standard basis sets given in the text.

Heats of Formation

Experimental and computed heats of formation of 18 isolated (gas-phase) monomeric compounds are presented in Table II. The average error for Li/PM3 is 6.2 kcal/mol, compared with 18.9 kcal/mol for Li/MNDO. Note the remarkable improvement for molecules with lithium–carbon contacts, which are of major interest in organolithium chemistry (Li-alkyl, -aryl, -alkenyl, -alkynyl). Compounds with more electropositive elements (H, Be) are described better than Li/MNDO, and compounds with more electronegative contact atoms (N, O, Cl, F) equally well or slightly worse, with Li/PM3.

Geometries

In general, the accuracy of bond lengths—particularly C—Li bonds—is improved significantly with Li/

Table I. Lithium parameters for PM3.

| | |
|-----------|--------|
| U_{ss} | –5.300 |
| U_{pp} | –3.400 |
| ζ_s | 0.650 |
| ζ_p | 0.750 |
| β_s | –0.550 |
| β_p | –1.500 |
| g_{ss} | 4.500 |
| g_{sp} | 3.000 |
| g_{pp} | 5.250 |
| g_{p2} | 4.500 |
| h_{sp} | 0.150 |
| α | 1.255 |
| K1(FN11) | –0.450 |
| L1(FN21) | 5.000 |
| M1(FN31) | 1.000 |
| K2(FN12) | 0.800 |
| L2(FN22) | 6.500 |
| M2(FN32) | 1.000 |

Table II. Heats of formation ΔH_f (kcal/mol) of the reference compounds.

| Formula | ΔH_f^{298} (kcal/mol) ref. | PM3 calc. | Difference PM3 | Difference MNDO | Ref. |
|------------------------------------|------------------------------------|-----------|----------------|-----------------|------|
| LiH | 33.6 \pm 0.2 | 41.6 | +8.0 | -10.4 | a |
| LiBeH | 75.8 \pm 1.0 | 80.1 | +4.3 | -38.5 | b |
| LiCH ₃ | 25.2 \pm 1.0 | 25.6 | +0.4 | -26.6 | b |
| LiNH ₂ | 8.4 \pm 1.0 | 19.6 | +11.2 | -0.8 | b |
| LiOH | -56.0 \pm 1.5 | -49.1 | +6.9 | +1.5 | a |
| LiF | -81.5 \pm 1.5 | -67.7 | +13.8 | -2.4 | c |
| Li ₂ | 51.6 \pm 0.7 | 66.3 | +14.7 | +4.0 | a |
| LiNC | 32.6 \pm 2.5 | 44.5 | +11.9 | +7.3 | d |
| LiOCH ₃ | -53.9 \pm 2.0 | -47.6 | +6.3 | -4.9 | e |
| Li ₂ O | -39.9 \pm 2.5 | -40.7 | -0.8 | +4.7 | a |
| LiCl | -46.8 \pm 3.0 | -48.0 | -1.2 | +8.3 | a |
| LiC ₂ H ₅ | 26.2 \pm 2.0 | 21.7 | -4.5 | -37.9 | b |
| Li-i-C ₃ H ₇ | 24.4 \pm 2.0 | 16.3 | -8.1 | -44.7 | b |
| Li-t-C ₄ H ₉ | 21.2 \pm 2.0 | 10.6 | -10.6 | -47.0 | b |
| LiC ₆ H ₅ | 54.7 \pm 3.0 | 55.7 | +1.0 | -35.0 | d |
| LiCH=CH ₂ | 49.7 \pm 3.0 | 47.4 | -2.3 | -35.4 | e,f |
| LiC \equiv CH | 64.9 \pm 2.5 | 66.7 | +1.8 | -24.7 | f |
| Li ⁺ | 164.2 \pm 0.5 | 160.6 | -3.6 | -7.5 | a |
| Errors | | | | | |
| Average unsigned | | | 6.2 | 18.9 | |
| Average signed | | | 2.8 | -16.1 | |
| rms | | | 7.7 | 25.0 | |

^aSee ref. 18.^bSee ref. 14.^cSee ref. 15.^dMP2/6-31G**//MP2/6-31G*.^eMP4(SDTQ)/6-31+G**//6-31+G*.^fSee ref. 16.

PM3 compared to Li/MNDO. This also holds for molecules with contacts of lithium to electronegative elements (Table III; in general, the reference data are based on high-level *ab initio* calculations). The av-

erage difference between reference and computed bond lengths of 17 molecules is 0.068 Å (0.167 Å) for Li/PM3 (Li/MNDO). Bond angles are reproduced slightly better with the new parameter set.

Table III. Bond lengths (Å) of the reference compounds.

| Formula | Bond lengths (Å) ref. | PM3 calc. | Difference PM3 | Difference MNDO | Ref. |
|------------------------------------|-----------------------|-----------|----------------|-----------------|------|
| LiH | 1.595 | 1.540 | -0.055 | -0.219 | a |
| LiBeH | 2.428 | 2.126 | -0.302 | -0.326 | b |
| LiCH ₃ | 2.004 | 1.926 | -0.078 | -0.183 | b |
| LiNH ₂ | 1.755 | 1.748 | -0.007 | -0.002 | b |
| LiOH | 1.600 | 1.576 | -0.024 | +0.031 | a |
| LiF | 1.563 | 1.586 | +0.023 | +0.051 | a |
| Li ₂ | 2.673 | 2.482 | -0.191 | -0.619 | a |
| LiNC | 1.775 | 1.796 | +0.021 | -0.018 | b |
| LiOCH ₃ | 1.599 | 1.593 | -0.006 | +0.073 | b |
| Li ₂ O | 1.590 | 1.604 | +0.014 | +0.051 | a |
| LiCl | 2.022 | 1.884 | -0.138 | +0.169 | a |
| LiC ₂ H ₅ | 2.024 | 1.962 | -0.062 | -0.195 | b |
| Li-i-C ₃ H ₇ | 2.037 | 1.985 | -0.052 | -0.197 | b |
| Li-t-C ₄ H ₉ | 2.041 | 2.017 | -0.024 | -0.180 | b |
| LiC ₆ H ₅ | 1.988 | 1.938 | -0.050 | -0.191 | c |
| LiCH=CH ₂ | 1.971 | 1.898 | -0.073 | -0.187 | b |
| LiC \equiv CH | 1.891 | 1.856 | -0.035 | -0.147 | b |
| Errors | | | | | |
| Average unsigned | | | 0.068 | 0.167 | |
| Average signed | | | -0.061 | -0.123 | |
| rms | | | 0.101 | 0.219 | |

^aSee ref. 18.^bMP2/6-31+G**//MP2/6-31+G**.^cMP2/6-31G**//MP2/6-31G*.

Table IV. Dipole moments (D) of the reference compounds.

| Formula | Dipole moments (D) ref. | PM3 calc. | Difference PM3 | Difference MNDO |
|------------------------------------|-------------------------|-----------|----------------|-----------------|
| LiH | 5.79 | 5.73 | -0.06 | -0.03 |
| LiBeH | 5.07 | 6.04 | +0.97 | +1.35 |
| LiCH ₃ | 5.71 | 5.19 | -0.52 | -0.08 |
| LiNH ₂ | 4.86 | 3.70 | -1.16 | -0.48 |
| LiOH | 4.53 | 3.08 | -1.45 | -0.85 |
| LiF | 6.54 | 5.32 | -1.22 | -0.84 |
| LiNC | 9.28 | 8.24 | -1.04 | -1.92 |
| LiOCH ₃ | 5.02 | 3.86 | -1.16 | +0.13 |
| LiCl | 7.39 | 6.54 | -0.85 | +0.40 |
| LiC ₂ H ₅ | 5.71 | 5.42 | -0.29 | -0.11 |
| Li-i-C ₃ H ₇ | 5.92 | 5.28 | -0.64 | -0.53 |
| Li-t-C ₄ H ₉ | 6.33 | 5.63 | -0.70 | -0.60 |
| LiC ₆ H ₅ | 6.29 | 5.99 | -0.30 | -0.20 |
| LiCH=CH ₂ | 5.98 | 4.91 | -1.07 | -0.94 |
| LiC≡CH | 6.08 | 5.53 | -0.55 | -0.73 |
| Errors | | | | |
| Average unsigned | | | 0.798 | 0.613 |
| Average signed | | | -0.599 | -0.360 |
| rms | | | 0.888 | 0.796 |

Table V. Ionization potentials (eV).

| Formula | Ionization pot. (eV) ref. ^a | PM3 calc. | Difference PM3 | Difference MNDO |
|----------------------------------|--|-----------|----------------|-----------------|
| Li ^b | 5.39 | 5.30 | -0.09 | -0.26 |
| Li ₂ ^b | 5.11 | 5.39 | +0.28 | -0.64 |
| LiH ^b | 7.7 | 8.70 | +1.00 | +0.55 |
| Li ₂ O ^b | 6.19 | 9.20 | +3.01 | +2.42 |
| LiCl ^b | 9.57 | 9.68 | +0.11 | +1.45 |
| Li ₂ Cl ₂ | 10.20 | 9.77 | -0.43 | +1.04 |
| Li ₃ Cl ₃ | (10.17) | 9.99 | -0.18 | +1.55 |
| LiO | (8.45) | 10.78 | +2.33 | +2.43 |
| Li ₂ O ₂ | (7.88) | 9.06 | +1.18 | -0.95 |
| LiBr | (8.7) | 12.58 | +3.88 | +0.83 |
| LiI | (7.5) | 8.82 | +1.32 | +1.23 |
| Li ₂ SiO ₃ | 8.3 | 7.96 | -0.34 | -0.29 |
| Errors | | | | |
| Average unsigned | | | 1.179 | 1.136 |
| Average signed | | | 1.006 | 0.780 |
| rms | | | 1.686 | 1.333 |

^aSee ref. 18.^bCompound included in optimization.

Dipole Moments and Ionization Potentials

Dipole moments (Table IV) are compared with MP2/6-31 + G**//MP2/6-31 + G** *ab initio* values, with a single exception.* The average Li/PM3 error for 15 compounds is 0.798 D vs. 0.613 D for Li/MNDO. First ionization potentials (Table V) were calculated for 12 compounds (5 of them included in the parameterization), but only 7 of the 12 experimental IPs are considered reliable.¹⁹ The mean deviation for all 12 molecules for Li/PM3 (Li/MNDO) is 1.179 eV (1.136 eV) and for those involved in the optimization 0.898 eV (1.064 eV).

*The dipole moment for phenyl lithium was calculated at the MP2/6-31G**//MP2/6-31G* level.

APPLICATIONS

We assessed the reliability of the new parameter set in predicting the structures and energies for: (1) the oligomerization of methyl lithium; (2) the structures and relative energies of the isomers of monolithiated dimethyl sulfone; (3) the activation energies for several lithiation reactions (e.g., of CO₂, formaldehyde, CH₄, and ethyne with lithium hydride and with methyl lithium); (4) the heats of formation and structures of some inorganic compounds; (5) the various bonding modes in benzyl lithium; and, finally, (6) the comparison of Li/MNDO and Li/PM3 structures with X-ray results of dimeric complexes in the [{4-(CH₃CR)C₅H₄N}Li]₂ series, with TMEDA or THF as polar ligands.

Table VI. Oligomerization of methyl lithium.

| Reaction | ΔH_R (kcal/mol) <i>ab initio</i> ^a | PM3 calc. | MNDO calc. |
|---|---|-----------|------------|
| 2LiCH ₃ → (LiCH ₃) ₂ (<i>C</i> _{2h}) | -46.6 | -58.8 | -72.2 |
| 3LiCH ₃ → (LiCH ₃) ₃ (<i>C</i> _{3h}) | -93.1 | -103.9 | -127.7 |
| 4LiCH ₃ → (LiCH ₃) ₄ (<i>T</i> _d) | -151.6 | -172.1 | -207.5 |
| 4LiCH ₃ → (LiCH ₃) ₄ (<i>C</i> _{4h}) | -133.1 | -140.0 | -182.6 |

| Structure | C—Li bond lengths (Å) | PM3 calc. | MNDO calc. |
|--|-----------------------|-------------|-------------|
| LiCH ₃ (<i>C</i> _{3v}) | 2.004 | 1.929 | 1.821 |
| (LiCH ₃) ₂ (<i>C</i> _{2h}) | 2.105/2.128 | 2.099/2.100 | 2.040/2.041 |
| (LiCH ₃) ₃ (<i>C</i> _{3h}) | 2.022/2.093 | 2.051/2.069 | 2.005/2.020 |
| (LiCH ₃) ₄ (<i>T</i> _d) | 2.188 | 2.241 | 2.197 |
| (LiCH ₃) ₄ (<i>C</i> _{4h}) | 1.985/2.075 | 2.040/2.057 | 1.996/2.009 |

^aMP2/6-31 + G**//MP2/6-31 + G*; zero point energies (6-31 + G*) scaled by 0.91 (see ref. 46).

Oligomerization of Methyl Lithium

The oligomerization energies, structures and bond lengths of di-, tri- and tetrameric methyl lithium³¹ are summarized in Table VI. Because of the better description of the C—Li interaction by Li/PM3 compared to Li/MNDO, the energies are computed much better. The same is true of the C—Li bond lengths in various oligomers, where Li/PM3 reproduces the reference values almost exactly. The C—Li bond is slightly too long only in the tetrahedral tetramer.

Table VII. Lithiated dimethyl sulfones.

| | Relative energies (kcal/mol) | | |
|----------|-------------------------------|-------|-------|
| | <i>Ab initio</i> ^a | PM3 | MNDO |
| 1 | 0.0 | 0.0 | 0.0 |
| 2 | +1.1 | +0.1 | +22.3 |
| 3 | +10.3 | +15.1 | +6.3 |
| 4 | — | +15.2 | +16.9 |

| Selected geometric parameters of lithium salt structures ^b | | | |
|---|-------------------------------|----------------------|----------------------|
| | <i>Ab initio</i> ^a | PM3 | MNDO |
| 1 | | | |
| S—C _a /S—C | 1.684/1.767 | 1.662/1.796 | 1.858/1.804 |
| S—O ₁ /S—O ₂ | 1.500/1.446 | 1.604/1.484 | 1.572/1.535 |
| Li—O ₁ /Li—O ₂ | 1.816/3.374 | 1.914/3.749 | 2.067/3.771 |
| Li—C _a | 2.170 | 2.223 | 1.992 |
| S—C _a —Li | 78.5 | 84.3 | 87.0 |
| O—S—O | 115.2 | 113.8 | 111.5 |
| 2 | | | |
| S—C _a /S—C | 1.605/1.773 | 1.528/1.797 | 1.659/1.832 |
| S—O | 1.501 | 1.594 | 1.571 |
| Li—O | 1.879 | 1.954 | 2.076 |
| Li—C _a | 3.519 | 3.802 | 3.882 |
| S—C _a —Li | 34.0 | 30.7 | 36.4 |
| O—S—O | 104.5 | 96.6 | 97.8 |
| 3 | | | |
| S—C _a /S—C | 1.674/1.761 | 1.673/1.779 | 1.910/1.788 |
| S—O | 1.470 | 1.556 | 1.566 |
| Li—O | 2.273 | 2.477 | 2.354 |
| Li—C _a | [2.000] ^c | [2.000] ^c | [2.000] ^c |
| S—C _a —Li | 74.1 | 80.7 | 76.0 |
| O—S—O | 111.6 | 108.0 | 102.4 |

^a3-21 + G(*)//3-21 + G(*).

^bBond lengths in Å, bond angles in degrees.

^cBond lengths fixed at 2.000 Å.

Both semiempirical and *ab initio* calculations predict the eclipsed arrangement of each methyl group above an Li₃ surface to be preferred over the staggered conformation.³²

Lithiated Dimethyl Sulfone

One of the most important features of PM3 is the improved description of hypervalent molecules, e.g., sulfur compounds. Therefore, it seemed useful to test the applicability of the new parameters for lithiated molecules containing hypervalent centers. Lithiated sulfones have been investigated both experimentally^{33–36} and theoretically.³⁷ Based on the latter, energies and geometries of monolithiated dimethyl sulfone isomers were calculated with Li/PM3 and compared with Li/MNDO and the *ab initio* results. An *ab initio* investigation has reported on three different structures **1–3** of dimethyl sulfone monolithium salts (Fig. 1). The relative energies and some selected bond lengths and angles are presented in Table VII. It should be noted that structure **3** was not fully optimized; the C—Li distance was fixed at 2.000 Å.³⁷ When fully optimized using PM3, **3** collapses into the global minimum **1**. Both semiempirical methods find an additional minimum **4**, which also is included in Table VII, and Figure 1.

Relative energies are reproduced poorly by Li/MNDO. Structure **2** should be approximately equal in energy to **1**, but it is found to be 21 kcal/mol less stable. In contrast to MNDO, PM3 reproduces the relative energy ordering of **1–3** correctly. Further, in agreement with the *ab initio* results,* the energy difference between **1** and **2** is small (0.1 kcal/mol). Structure **4**, for which no *ab initio* data are available, is predicted to be about 5 kcal/mol lower in energy than **2** by Li/MNDO. This results from the overestimation of C—Li interaction with the Li/MNDO

Further investigations³⁸ show that the relative energies and geometries given in ref. 37 are reliable despite the relatively low basis set [3-21 + G()]. At the MP2/6-31 + G**//MP2/6-31 + G* level, the energy differences compared to structure **1** are +5.1 and +6.7 kcal/mol for **2** and **3**, respectively.

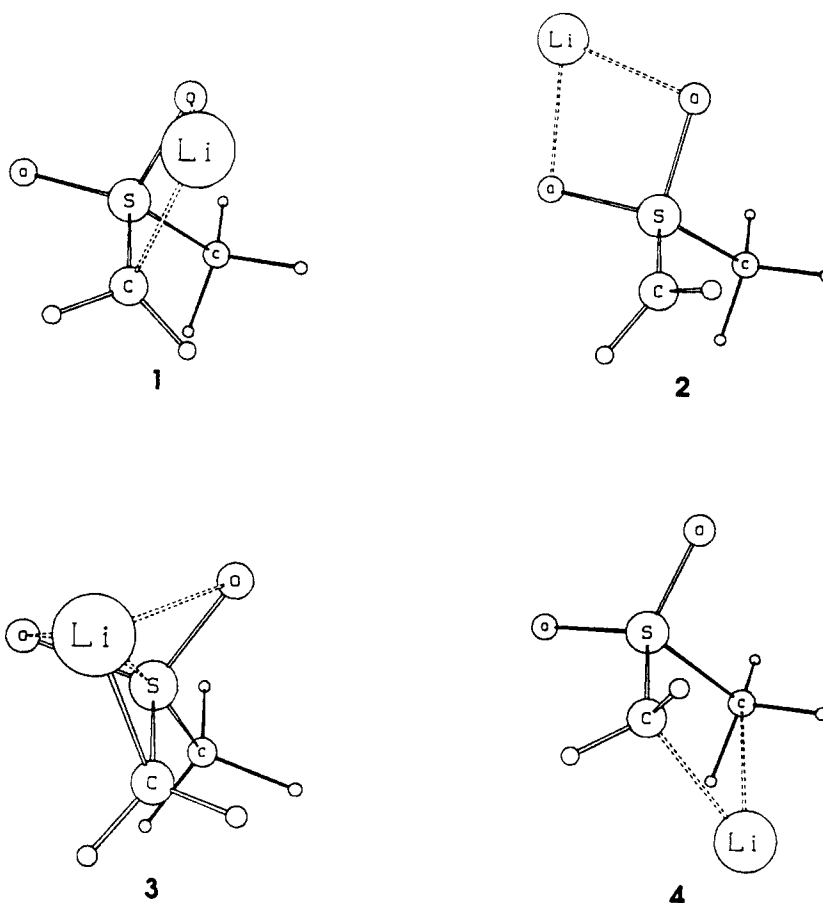


Figure 1. Isomers of monolithiated dimethyl sulfone, $[\text{CH}_3\text{—SO}_2\text{—CH}_2]^- \text{Li}^+$; Li/PM3 results. For *ab initio* calculations see ref. 37.

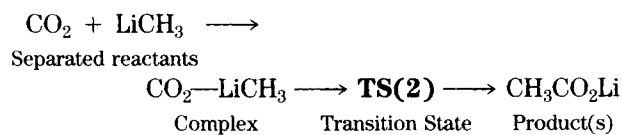
method. Li/PM3 predicts **4** to be the least stable isomer.

Comparison of the Li/PM3-optimized structures with *ab initio* data reveals good agreement. Only S—O bond lengths (~ 0.1 Å too long) and the “free” S—C_a bond in **2** (no lithium associated to S or C, ~ 0.07 Å too short) are not reproduced accurately. Calculation of the (methylsulfonyl)-methyl anion reveals an S—O bond that is 0.07 Å too long and an S—C_a bond that is 0.06 Å too short. Therefore, both these errors are inherent to PM3, and do not result from the lithium parameterization. Li/MNDO optimizations describe these structures far less accurately. Note that the S—C_a bond is elongated to a larger extent than the S—C bond when lithium cation is coordinated.

Transition Structures and Activation Energies

Apart from computing reactants and products correctly, the parameters also should allow the calculation of transition states, i.e., the estimation of activation barriers. Based on previously published theoretical investigations, several reactions including transition structures were recalculated. Carboxylation of lithium hydride and methyl lithium,³⁹ addition of formaldehyde to lithium hydride,⁴⁰ and the

reaction of lithium hydride with methane and ethyne⁴¹ were chosen as model reactions. All of them have the same features as exemplified by the CO₂/LiCH₃ system (Table VIII):



While the error in activation energies is comparable for both semiempirical methods, most of the Li/PM3-calculated bond lengths of the transition

Table VIII. Transition states.

| Reaction | Activation energies (kcal/mol) | | |
|---|--------------------------------|-------|-------|
| | <i>Ab initio</i> | PM3 | MNDO |
| CO ₂ + LiH → HCOOLi | +1.5 ^a | +7.6 | +4.0 |
| CO ₂ + LiCH ₃ → CH ₃ COOLi | +0.9 ^b | +9.3 | +15.9 |
| HCHO + LiH → CH ₃ OLi | +3.0 ^c | +8.5 | +4.3 |
| CH ₄ + LiH → CH ₃ Li + H ₂ | +29.1 ^d | +17.7 | +33.4 |
| HCCH + LiH → HCCLi + H ₂ | +10.2 ^e | +11.7 | +24.9 |

^aMP2/6-31 + G**//MP2/6-31G*, ref. 39.

^bMP2/6-31G*//6-31G*, ref. 39.

^cMP2/6-31 + G**//6-31G*, ref. 40.

^dMP2/6-31 + + G**//6-31 + + G**, ref. 41.

^eMP2/6-31 + + G**//6-31G*, ref. 41.

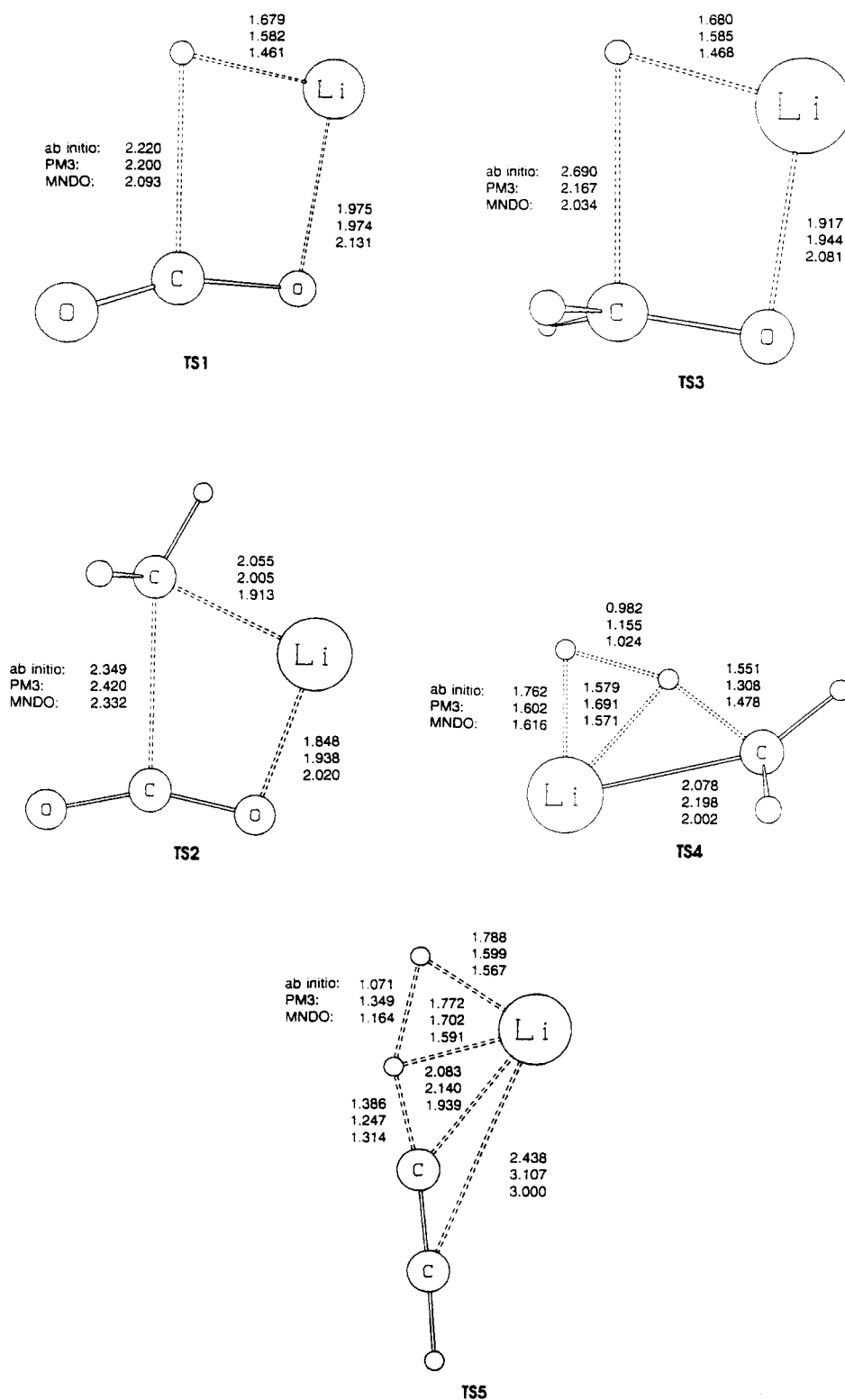


Figure 2. Bond lengths (Å) of selected transition states.

structures agree better with *ab initio* results (Fig. 2). This is most pronounced in the case of oxygen-containing structures: Li—O, Li—H, and Li—C distances are calculated with greater accuracy. However, Li/MNDO seems to be superior for the CH₄/LiH system.

Inorganic Lithium Compounds

Li/PM3 does not perform better than Li/MNDO in all respects. There are some deficiencies of Li/PM3, especially for some small inorganic molecules such as summarized in Table IX. In general, the accuracy

Table IX. Inorganic lithium compounds.

| Formula | Variable | Exp. ^a | PM3 | MNDO |
|---------------------------------|-------------------------|-------------------|-------------|-------------|
| Li ₂ F ₂ | ΔH_f (kcal/mol) | -225.3 ± 4 | -181.8 | -254.8 |
| | Bond length (Å) | 1.68 | 1.782 | 1.841 |
| | Bond angle (°) | 74.8/105.2 | 77.0/103.0 | 82.8/97.2 |
| Li ₃ F ₃ | ΔH_f (kcal/mol) | -362.6 ± 6 | -286.7 | -414.6 |
| | Bond length (Å) | 1.68 | 1.782 | 1.829 |
| | Bond angle (°) | 120/120 | 116.2/123.8 | 118.5/121.5 |
| Li ₂ Cl ₂ | ΔH_f (kcal/mol) | -143.1 ± 3 | -165.2 | -116.5 |
| | Bond length (Å) | 2.23 | 2.113 | 2.473 |
| | Bond angle (°) | 72/108 | 76.8/103.3 | 70.3/109.7 |
| Li ₃ Cl ₃ | ΔH_f (kcal/mol) | -240.1 ± 5 | -273.7 | -186.5 |
| | Bond length (Å) | (2.2) | 2.075 | 2.448 |
| | Bond angle (°) | 120/120 | 111.3/128.7 | 92.8/147.2 |
| LiCl ⁺ | ΔH_f (kcal/mol) | 174 | 164.0 | 182.7 |
| LiBr | ΔH_f (kcal/mol) | -36.8 ± 3 | -54.0 | -14.6 |
| | Bond length (Å) | 2.17 | 1.805 | 2.312 |
| Li ₂ Br ₂ | ΔH_f (kcal/mol) | -119.7 ± 5 | -136.0 | -65.6 |
| | Bond length (Å) | 2.35 | 2.130 | 2.593 |
| | Bond angle (°) | 70/110 | 70.6/109.4 | 68.1/111.9 |
| LiBr ⁺ | ΔH_f (kcal/mol) | (164) | 184.6 | 181.5 |
| LiI | ΔH_f (kcal/mol) | -21.7 ± 2 | -18.8 | -2.0 |
| | Bond length (Å) | 2.392 | 2.190 | 2.346 |
| Li ₂ I ₂ | ΔH_f (kcal/mol) | -86.5 ± 4 | -51.8 | -54.4 |
| | Bond length (Å) | 2.54 | 2.669 | 2.602 |
| | Bond angle (°) | 64/116 | 67.4/112.6 | 68.1/111.9 |
| LiO | ΔH_f (kcal/mol) | 20.1 ± 5 | 25.0 | 29.8 |
| | Bond length (Å) | 1.62 | 1.672 | 1.750 |
| Li ₂ O ₂ | ΔH_f (kcal/mol) | -58 ± 6 | -54.2 | -27.5 |
| | Bond length (Å) | 1.90 | 1.797 | 1.939 |
| | Bond angle (°) | 64/116 | 54.6/125.4 | 39.9/140.1 |

^aSee ref. 18.

of Li/PM3 for ΔH_f values of inorganic lithium halides is about the same as Li/MNDO; the results for the oxides are slightly better than Li/MNDO. For example, the heat of formation of trimeric lithium fluoride deviates significantly, 76 kcal/mol (Li/PM3) and 52 kcal/mol (Li/MNDO), from the experimental result. The Li—Br bond in LiBr is significantly too short, even shorter than the Li—Cl bond in LiCl. But, in general, Li/PM3 offers advantages for most compounds.

Benzyl Lithium System

Benzyl lithium (Table X) demonstrates the performance of the new parameter set further. Previous *ab initio*^{42–44} and Li/MNDO⁴⁵ calculations results in five stationary points, represented by the structures **5**, **6**, **8**, **9**, and **10**. Li/PM3 and *ab initio* investigations presented herein lead to an additional structure, **7** (Fig. 3).*

Ab initio methods predict the η^3 (C₁) isomer **5** to be the global minimum. The η^2 structure **8** is a tran-

Table X. Benzyl lithium isomers.

| | Selected bond lengths (Å) | | |
|-------------------------------------|-------------------------------|-------|-------|
| | <i>Ab initio</i> ^a | PM3 | MNDO |
| 5 | | | |
| C _{exo} —Li | 2.025 | 2.025 | 1.889 |
| C _{ipso} —Li | 2.171 | 2.421 | 2.230 |
| C _{ortho} —Li | 2.428 | 2.526 | 2.325 |
| C _{exo} —C _{ipso} | 1.454 | 1.451 | 1.495 |
| 6 | | | |
| C _{exo} —Li | — | 1.999 | — |
| C _{exo} —C _{ipso} | — | 1.455 | — |
| 7 | | | |
| C _{exo} —Li | 2.071 | 1.989 | 1.839 |
| C _{ipso} —Li | 3.045 | 2.735 | 2.466 |
| C _{ortho} —Li | 3.275 | 2.745 | 2.478 |
| C _{exo} —C _{ipso} | 1.520 | 1.477 | 1.519 |
| 8 | | | |
| C _{exo} —Li | 2.018 | — | 1.885 |
| C _{ipso} —Li | 2.194 | — | 2.176 |
| C _{exo} —C _{ipso} | 1.468 | — | 1.498 |
| 9 | | | |
| C ₁ —Li | 2.131 | 2.289 | 2.171 |
| C _{2,6} —Li | 2.189 | 2.355 | 2.230 |
| C _{3,5} —Li | 2.294 | 2.401 | 2.236 |
| C ₄ —Li | 2.525 | 2.544 | 2.323 |
| C _{exo} —C _{ipso} | 1.342 | 1.348 | 1.362 |
| 10 | | | |
| C _{exo} —Li | 2.544 | 2.592 | 2.292 |
| C _{ipso} —Li | 2.033 | 2.163 | 1.974 |
| C _{ortho} —Li | 2.305 | 2.464 | 2.364 |
| C _{exo} —C _{ipso} | 1.384 | 1.380 | 1.414 |

^a6-31G* geometries.

*Results of *ab initio* calculations (MP2/6-31 + G**/6-31G*). Energy, -277.47744 a.u. (C_s symmetry); zero point energy (6-31G*), 77.7 kcal/mol; number of imaginary frequencies, 1. With the ZPE correction, scaled with 0.91⁴⁶ transition state **7** is 10.5 kcal/mol less stable than the most stable η^3 structure **5** (ref. 44).

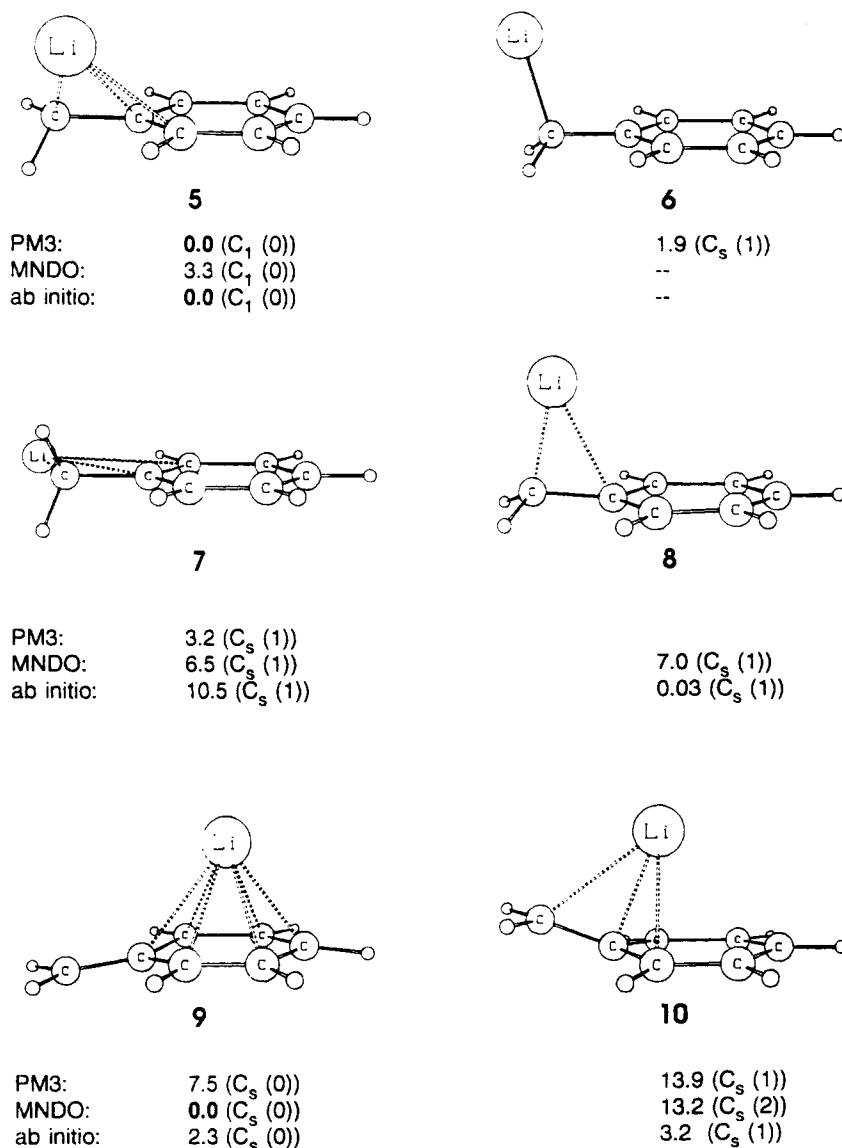


Figure 3. Relative energies (kcal/mol) of the isomers of benzyl lithium. Results of *ab initio* calculations, see ref. 44 (MP2/6-31 + G**/6-31G*, ZPE corrected). In brackets: Symmetry symbols and number of imaginary frequencies.

sition structure only slightly higher in energy than **5**. In the second minimum, **9** (η^5 , C_s), the lithium cation is located above the ring. The $\eta^1(C_s)$ and $\eta^3(C_s)$ isomers **7** and **10** are transition structures. Sygula and Rabideau modeled purely ionic behavior of the lithium cation by removing all the orbitals except 1s from the basis set and found structure **6** (η^1) to be the global minimum.^{43,47} This structure seems to be an artifact of the truncated basis set.*

Semiempirical calculations give the following results: *Ab initio* and Li/PM3 results agree in predicting the η^3 isomer **5** to be most stable, whereas Li/MNDO overestimates the stability of the η^6 structure **9**. With Li/MNDO, the η^1 structure **6** is not a stationary point; with Li/PM3, it is a transition state.

The preferred mode in PM3 for the interconversion of **5** into its mirror image is characterized by the movement of lithium cation *above* the $C_{\text{exo}}/C_{\text{ipso}}/C_{\text{ortho}}$ plane via **6**, which affords 1.9 kcal/mol. In contrast, Li/MNDO prefers the rotation of the LiCH_2 moiety around the $C_{\text{exo}}-C_{\text{ipso}}$ bond via the C_s -symmetrical transition structure **7** (activation energy, 6.5 kcal/mol) with the lithium cation *in* the $C_{\text{exo}}/C_{\text{ipso}}/C_{\text{ortho}}$ plane and disagrees with the *ab initio* results, which predict **8** to be the transition state for conversion of **5** [activation energy, 0.03 kcal/mol (MP2/6-31 + G**/6-31G*); Li/MNDO, 7.0 kcal/mol] into its mirror image.

Thus, Li/PM3 performs much better than Li/MNDO in predicting the relative energy order of these isomers and their transformation modes. However, compared with these Li/PM3 results, the *ab initio*-calculated potential energy surface for move-

*For a detailed discussion, see ref. 43 and the references cited.

ment of the lithium cation in the C_s plane (orthogonal to the ring) of benzyl lithium is much flatter. (Compare, e.g., the Li/PM3- and MP2/6-31 + G**//6-31G*-calculated relative energies of the transition structure **10** on the latter is not a stationary point in the Li/MNDO approximation). The Li—C bond lengths of all isomers are calculated with comparable accuracy by both semiempirical methods.

As pointed out previously on the basis of *ab initio* calculations,⁴⁴ the degree of the lithium coordination at the C_{exo} position parallels the elongation of the C_{exo} — C_{ipso} bond length. This trend is predicted by both Li/PM3 and Li/MNDO (Table X, structures **9**, **10**, **5**, and **7**; increasing lengths). Except for the transition structure **7**,* the Li/PM3 values agree better with the 6-31G* results than the Li/MNDO.

Comparison with X-Ray Structures of Dimeric $[4-(CH_3CR)C_5H_4N]Li_2$ TMEDA or THF Complexes

Finally, to test the reliability of the Li/PM3 method in predicting geometries of larger systems we have included compounds **11**, **12** (TMEDA complexes), and **13** (THF complex) in our study. The X-ray structures of these complexes have been reported recently.^{11,44} In the crystal, the TMEDA complex **12** (not the THF complex) shows a significant distortion from the idealized D_{2h} symmetry due to crystal packing effects and (to a minor extent) the steric demand of the TMEDA ligands. The Li/PM3 and Li/MNDO calculations were then performed assuming idealized geometries (D_2 symmetry for **11**, D_{2h} for **12** and **13**).[†] Figures 4 and 5 show the interatomic distances in the central Li/N/Li/N segments and of the N—Li or O—Li contacts to the coligands. Based on the X-ray results, all distances are described better by the Li/PM3 method.

Further, in the X-ray structures the bond lengths of the heterocyclic (anionic) moieties reveal the characteristics of *N*-substituted 4-alkylidene-1,4-dihydropyridines that are not affected significantly by the nature of the coligands. This structural property is reproduced much better by Li/PM3 results (Table XI). A systematic Li/PM3 error was observed for the N1—C2 bond lengths, which are calculated to be too long [average deviation: +0.038 Å (PM3), +0.016 Å (MNDO)].

*PM3—more than MNDO—underestimates C_{exo} — C_{ipso} bond lengths of systems with a C_{exo} lone pair coplanar to the phenyl ring system. A typical example is the free benzyl anion with the CH_2 moiety periplanar to the ring plane (C_s symmetry): 6-31G**//6-31G*, 1.477 Å; MP2/6-31 + G**//MP2/6-31 + G*, 1.475 Å; PM3, 1.412 Å; MNDO, 1.433 Å.

†Starting from different (nonrestricted) geometries of **12**, both semiempirical methods lead to the most stable D_{2h} structure.

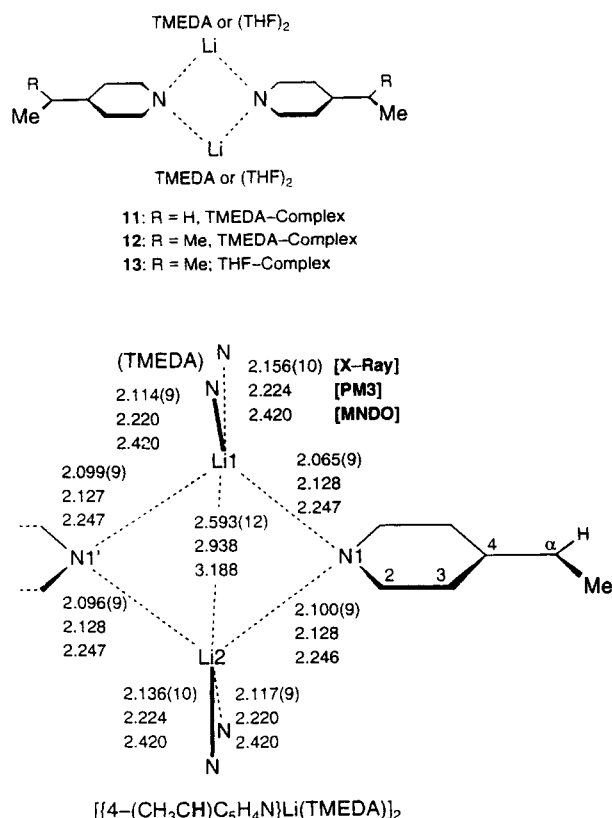
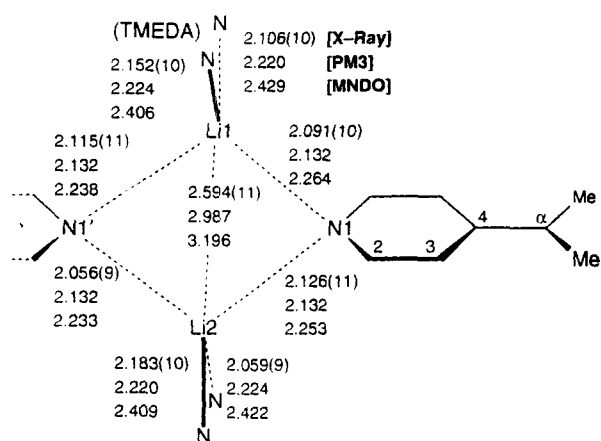


Figure 4. Comparison of selected bond lengths (Å) of a dimeric TMEDA-complex.

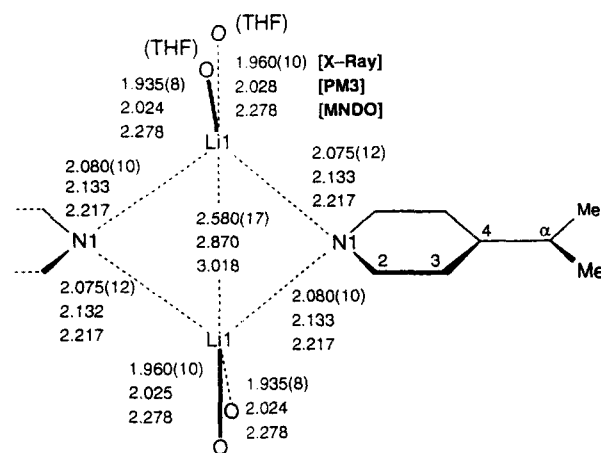
CONCLUSIONS

The examples discussed demonstrate some of the major improvements with the PM3 lithium parameters. Comparing the two semiempirical methods with experimental and *ab initio* computed structures as well as with thermochemical data shows Li/PM3 to be distinctly superior to Li/MNDO. The overestimation of the C—Li bond strength by Li/MNDO has been reduced significantly without worsening the performance for other types of bonds (see Table III). Several X-ray structures including lithiated heterocyclic compounds with different coligands (THF, TMEDA) were calculated using both semiempirical methods. In all cases, Li/PM3 reproduced the experimentally determined geometries better than Li/MNDO. Moreover, comparison of oligomerization energies for organolithium compounds also reveals the superiority of Li/PM3 over Li/MNDO. *Ab initio* and Li/PM3 (but not the Li/MNDO) results for the di-, tri-, and tetramerization energies of methyl lithium agree well.

With the introduction of this PM3 parameter set, a second popular semiempirical method is now available for calculating systems containing lithium. Because PM3 generally outperforms MNDO in many aspects, semiempirical calculations involving lithium compounds can now be extended to a wider range of chemical problems. The inclusion of various types



$[[4-(\text{CH}_3\text{CCH}_3)\text{C}_5\text{H}_4\text{N}]\text{Li}(\text{TMEDA})]_2$



$[[4-(\text{CH}_3\text{CCH}_3)\text{C}_5\text{H}_4\text{N}]\text{Li}(\text{THF})]_2$

Figure 5. Comparison of selected bond lengths (Å) of a dimeric TMEDA- and a THF-complex.

of organolithium compounds in this parameterization allows a more accurate treatment of important synthetic reagents with Li/PM3. We believe this is a major improvement to Li/MNDO, especially as it gives more reliable descriptions of molecules con-

taining hypervalent atoms and of molecular geometries in general. Although not all possible areas of special interest have been tested, we believe that a representative number of different types of molecules have been surveyed. Of course, this does not exclude the possibility of some failures of the new parameter set when applied to new areas.

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Table XI. Bond lengths (Å) of the ring systems.

| Bond (Å) | X-ray ^a | PM3 ^a | MNDO ^a |
|--|--------------------|------------------|-------------------|
| $[[4-[\text{CH}_3\text{CH}]\text{C}_5\text{H}_4\text{N}]\text{Li} \times \text{TMEDA}]_2$ | | | |
| N1—C2 | 1.370(7) | 1.415 | 1.393 |
| C2—C3 | 1.344(8) | 1.356 | 1.376 |
| C3—C4 | 1.442(9) | 1.452 | 1.468 |
| C4—C _{exo} | 1.354(8) | 1.352 | 1.366 |
| $[[4-[\text{CH}_3\text{CCH}_3]\text{C}_5\text{H}_4\text{N}]\text{Li} \times \text{TMEDA}]_2$ | | | |
| N1—C2 | 1.378(7) | 1.414 | 1.390 |
| C2—C3 | 1.343(8) | 1.357 | 1.377 |
| C3—C4 | 1.455(8) | 1.453 | 1.469 |
| C4—C _{exo} | 1.355(8) | 1.360 | 1.381 |
| $[[4-[\text{CH}_3\text{CCH}_3]\text{C}_5\text{H}_4\text{N}]\text{Li} \times (\text{THF})_2]_2$ | | | |
| N1—C2 | 1.377(7) | 1.413 | 1.390 |
| C2—C3 | 1.352(9) | 1.357 | 1.376 |
| C3—C4 | 1.465(7) | 1.452 | 1.468 |
| C4—C _{exo} | 1.362(8) | 1.360 | 1.381 |

^aAveraged values and deviations.

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