experimentally determined vibrational spectra of $Tl(CH_3)_2^+$ and TlBr. The calculated frequencies for $Tl(CH_3)_3$ are in good agreement with the measurements of Johnson and Downs. The vibrational spectra for the as yet unmeasured gas-phase structures of $TlCH_3$, $Tl(CH_3)_2Br$, and $Tl(CH_3)_4^-$ are predicted. Scaled HF frequencies may have deviations up to 10% compared to experiment but are certainly useful for the prediction of infrared and Raman data for organometallic compounds and the assignment of spectral bands, which would normally require the preparation of isotopically substituted molecules.

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# AM1 Parameters for Aluminum

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AM1 has been parametrized for aluminum. Calculations are reported for a number of molecules containing aluminum. The results are better than those given by the MNDO or PM3 models. The technique used by Stewart to parametrize PM3 is criticized.

## Introduction

Aluminum is an important element, in both chemistry and chemical technology. Organoaluminum compounds in particular have proved of major interest and value as catalysts and in organic synthesis. There is therefore a clear need for a theoretical treatment of aluminum compounds that could be used in conjunction with experiment to interpret their chemical behavior. As usual,[1] ab initio procedures are of limited value in this connection because of the computing time required by those of adequate accuracy.

This need has been met in organic chemistry by the parametric ("semiempirical") methods developed by our group, i.e., MINDO/3,[2] MNDO,[3] and AM1,[4] AM1 being the latest and most effective. Tests[5] have shown AM1 to give results comparable with those from ab initio methods that require thousands of times more computing time, and the calculations can be carried out very easily, comprehensive easy-to-use computer programs being freely available (AMPAC[6]). However, while MNDO parameters for aluminum have been available[7] for some time now and have proved useful,[8] the errors in the MNDO heats of formation ($\Delta H_f$) tend to be rather large. Furthermore, MNDO suffers from well-known deficiencies that have been overcome[4] in AM1.

We therefore decided to parametrize AM1 for aluminum. Here we report our results. In the meantime, Stewart has described[9] a new version of AM1 that he terms PM3 and that contains parameters for aluminum. Various points concerning this are discussed below.

## Procedure

The techniques used here to optimize the parameters in semiempirical treatments have been described in detail.[10] However, some further comment seems appropriate in view of two recent papers by Stewart[9,11] describing a procedure that he claims to be simpler and more effective than the one developed by our group.

Optimization of parameters involves minimization of an error function (SSQ) consisting of a sum of the squares of the weighted errors in various properties of a selected *basis set* of molecules. In our approach, the basis set consists of a limited number of molecules and properties, chosen to provide a balanced sample of the various known types. The weighting factors and the properties and molecules in the basis set are determined by trial, the choice being based on the chemical acceptability of the results for as many additional molecules and properties as the available data will allow. A further problem is the fact that the *parameter hypersurface*, defining SSQ as a function of the parameters, has numerous minima. The minimum reached in a given optimization depends on the initial values assumed for the parameters. Since there is no way to tell whether or not a given minimum is the optimum one and since there is no systematic way to escape from one minimum to another, parametrization can involve an enormous amount of computation.

Stewart, on the other hand, claims[9,11] that optimum results can be obtained by a single minimization if enough molecules and properties are included in the basis set. According to this view, parametrization can be made

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(1) (a) Dewar, M. J. S. *Int. J. Quantum. Chem.* **1988**, *22*, 557. (b) Dewar, M. J. S.; Jie, C. *J. Chem. Soc., Chem. Commun.* **1989**, 98. (c) Dewar, M. J. S.; Holder, A. *Heterocycles* **1989**, *28*, 1135. (d) Dewar, M. J. S.; Jie, C. *J. Am. Chem. Soc.* **1989**, *111*, 511.

(2) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285, 1294, 1302, 1307.

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(6) Quantum Chemistry Program Exchange, Indiana University, Chemistry Department, Bloomington, Indiana 47405, as QCPE No. 506.

(7) Davis, L. P.; Guidry, R. M.; Williams, J. R.; Dewar, M. J. S.; Rzepa, H. S. *J. Comput. Chem.* **1981**, *2*, 433.

(8) Dieter, K. M.; Dymek, Jr., C. J.; Heimer, N. E.; Rovang, J. W.; Wilkes, J. S. *J. Am. Chem. Soc.* **1988**, *110*, 2722.

(9) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209.

(10) Dewar, M. J. S. *J. Mol. Struct.* **1983**, *100*, 41.

(11) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 221.

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**Table I. AM1 Parameters for Aluminum, with MNDO[a] and PM3[b] Values for Comparison**

| parameter | AM1 | PM3 | MNDO |
|---|---|---|---|
| $U_{ss}$, eV | −24.353585 | −24.845404 | −23.807097 |
| $U_{pp}$, eV | −18.363645 | −22.264159 | −17.519878 |
| $\zeta_s$, au | 1.516593 | 1.702888 | 1.444161 |
| $\zeta_p$, au | 1.306347 | 1.073629 | |
| $\beta_s$, eV | −3.866822 | −0.594301 | −2.670284 |
| $\beta_p$, eV | −2.317146 | −0.956550 | |
| $\alpha$, Å$^{-1}$ | 1.976586 | 1.521703 | 1.868839 |
| intensity, eV | | | |
| no. 1 | 0.090000 | −0.473090 | |
| no. 2 | | −0.154051 | |
| width, Å$^2$ | | | |
| no. 1 | 12.392443 | 1.915825 | |
| no. 2 | | 6.005086 | |
| position, Å | | | |
| no. 1 | 2.050394 | 1.451728 | |
| no. 2 | | 2.51997 | |

[a] See ref 7. [b] See ref 11.

wholly automatic if enough data are used. Stewart justifies this approach by his use of it in the development[9] of a new version (PM3) of AM1 that he claims to be superior to AM1 itself. However, since Stewart had the AM1 parameters available as a starting point, he had no problems in finding a good minimum on the parameter hypersurface or suitable values for the weighting factors for different molecular properties. The only occasion on which his approach has been tried a priori was in his original attempt to develop AM1, which failed.[12] AM1 was in fact developed by Zoebisch, using the approach pioneered here. A full account will be found in ref 13. These remarks refer to the original parametrization of AM1 for the "organic" elements (C, H, O, N). Stewart's approach is likely to be even less effective in other cases because of the lack of thermochemical data for compounds of most other elements. As will appear presently, the results reported here support this conclusion in the case of aluminum.

Stewart's approach is also inherently dubious because it uses an arbitrary basis set of molecules, namely, those for which experimental data happen to be available. Under these conditions, some kinds of molecule are likely to be overrepresented and others are underrepresented. Furthermore, in cases where the experimental data are limited, all available molecules are likely to be included in the parametrization. There is then no independent check on the general validity of the results. Unless a procedure has been shown to reproduce properties of molecules not used in the parametrization, it cannot safely be extrapolated to such situations.

In parametrizing additional elements in our approach, the values for previously parametrized elements are retained. As before,[4] the properties used for parametrizing aluminum included heats of formation, dipole moments, ionization potentials, and molecular geometries. The calculations were carried out using the standard AM1 method as implemented in the AMPAC program.[6] Calculations for radicals were carried out using the "half-electron" method.[14]

**Table II. Comparison of Calculated (AM1) and Observed[a] Heats of Formation[b] for Compounds Containing Aluminum and of Errors for AM1, MNDO, and PM3**

| | heat of formation | | error in heat of formation | | |
|---|---|---|---|---|---|
| species | exptl | AM1 | AM1 | MNDO | PM3 |
| $Al^+$ | 218.1 | 213.3 | −4.8 | −24.2 | 61.7 |
| $Al_2$ | 116.4 | 120.0 | 3.6 | 14.9 | −36.8 |
| $AlBr^{*g}$ | 3.8 | −0.3 | −4.1 | −3.1 | 1.2 |
| $AlBr_3$ | −98.1 | −96.4 | 1.7 | 12.3 | 37.8 |
| $Al_2Br_6$ | −223.9 | −248.9 | −25.0 | 91.4 | −0.9 |
| $AlCl^{\bullet +}$ | 204.5 | 180.1 | −24.4 | −31.2 | −7.3 |
| AlCl | −12.3 | −20.9 | −8.6 | −15.5 | 6.8 |
| $AlCl_2^+$ | 115.0 | 104.2 | −10.8 | 3.9 | 9.3 |
| $AlCl_2^{\bullet}$ | −67.0 | −74.0 | −7.0 | −7.6 | −1.2 |
| $AlCl_2^-$ | −115.0 | −119.9 | −4.9 | −15.6 | −30.0 |
| $AlCl_3*$ | −139.4 | −140.3 | −0.9 | −0.6 | 17.6 |
| $Al_2Cl_6*$ | −309.6 | −318.4 | −8.8 | 14.4 | −1.5 |
| $AlF^{\bullet +}$ | 164.0 | 127.0 | −37.0 | −50.6 | −5.0 |
| AlF | −63.5 | −77.9 | −14.4 | 13.4 | −50.1 |
| $AlF_2^+$ | 22.0 | 18.4 | −3.6 | −7.8 | 7.0 |
| $AlF_2^{\bullet}$ | −166.0 | −169.0 | −3.0 | −5.1 | 3.3 |
| $AlF_2^-$ | −217.0 | 223.1 | 6.1 | 7.4 | −12.6 |
| $AlF_3*$ | −289.0 | −285.8 | 3.2 | −2.3 | −2.5 |
| $AlF_4^{-c}$ | −469.4 | −427.7 | 41.7 | 35.4 | 6.8 |
| $Al_2F_6*$ | −629.5 | −624.2 | 5.3 | −2.1 | −1.9 |
| AlI | 16.2 | 29.0 | 12.8 | 15.0 | 33.1 |
| $AlI_3*$ | −46.2 | −29.7 | 16.5 | 57.8 | 6.3 |
| $Al_2I_6$ | −117.0 | −107.4 | 9.6 | 124.4 | −0.4 |
| $AlClF^+$ | 66.0 | 60.8 | −5.2 | −2.5 | −8.9 |
| $AlClF^{\bullet}$ | −117.0 | −120.5 | −3.5 | −7.7 | 1.0 |
| $AlCl_2F$ | −189.0 | −186.7 | 2.3 | −2.4 | 11.0 |
| $AlClF_2$ | −238.8 | −236.2 | 2.6 | −2.8 | 4.2 |
| AlClO* | −82.2 | −66.4 | 15.8 | 14.5 | 10.8 |
| AlFO | −139.0 | −110.1 | 28.9 | 25.4 | 14.3 |
| $AlF_2O$ | −313.0 | −257.2 | 55.8 | 53.7 | 25.6 |
| AlH* | 62.2 | 52.9 | −9.3 | −16.0 | 8.1 |
| AlN* | 125.0 | 117.9 | −7.1 | 15.9 | −49.5 |
| $AlO^-$ | −62.9 | −52.9 | 10.0 | 8.6 | 13.5 |
| $AlO^{\bullet}$ | 16.0 | 8.4 | −7.6 | −17.8 | −23.9 |
| $AlO^+$ | 237.7 | 240.8 | 3.1 | −14.2 | −34.9 |
| $AlO_2^{\bullet}$ | −20.6 | −3.9 | 16.7 | 6.2 | −37.4 |
| $AlO_2^-$ | −115.0 | −95.4 | 19.6 | 25.5 | −1.1 |
| $Al_2O^{\bullet +}$ | 159.4 | 148.4 | −11.0 | −46.8 | 12.6 |
| $Al_2O$ | −34.7 | −39.2 | −4.5 | −37.0 | 6.1 |
| $Al_2O_2^{\bullet +}$ | 126.0 | 127.1 | 1.7 | −47.1 | −53.5 |
| $Al_2O_2$ | −94.3 | −75.4 | 18.9 | −13.5 | 6.8 |
| $AlOH^{\bullet +}$ | 130.0 | 158.0 | 28.0 | 59.2 | −0.7 |
| AlOH* | −43.0 | −40.1 | 2.9 | 9.6 | −33.4 |
| $AlOH^{\bullet -}$ | −55.0 | −44.7 | 10.3 | 13.9 | −50.7 |
| HAlO | 9.0 | −21.9 | −30.9 | −13.7 | 10.2 |
| $AlO_2H$ | −109.0 | −79.5 | 29.5 | 16.2 | 4.9 |
| $AlS^d$ | 48.0 | 34.4 | −13.6 | 4.6 | −16.6 |
| $Al(CH_3)_3^{*e}$ | −20.9 | −27.4 | −6.5 | −19.2 | 15.2 |
| $Al(C_2H_5)_3^{*f}$ | −39.0 | −46.2 | −7.2 | −16.0 | 4.6 |
| $Al(C_3H_7)_3^{*f}$ | −57.2 | −66.6 | −9.4 | −11.4 | 10.3 |
| av absolute | | | 12.39 | 21.55 | 16.22 |
| av signed | | | 1.35 | −0.11 | 0.07 |
| no. of examples | | | 50 | | |

[a] Unless otherwise noted: Chase, Jr., M. W.; Davies, C. A.; Downey, Jr., J. R.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *JANAF Thermochemical Tables*, 3rd ed.; American Chemical Society: Washington, D.C., 1986; Part I. [b] Units: kcal/mol. [c] Farber, M.; Srivastava, R. V. *High Temp. Sci.* **1979**, *11*, 1. [d] Chase, Jr., M. W.; Davies, C. A.; Downey, Jr., J. R.; McDonald, R. A.; Syverud, A. N. *JANAF Thermochemical Tables*, 3rd ed, *J. Phys. Chem. Ref. Data, Suppl. 1* **1985**, 14. [e] Smith, M. B. *J. Organomet. Chem.* **1974**, *76*, 171. [f] Benson, S. W.; Francis, J. T.; Tsotsis, T. T. *J. Phys. Chem.* **1988**, *92*, 4515. [g] Asterisks denote molecules in parametrization basis set.

## Results and Discussion

**Parameters.** Table I lists the AM1 parameters for aluminum in the usual[3,4] notation, together with the values used in MNDO and PM3. The basic difference between MNDO and the two later procedures lies in the core re-

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(12) While the calculated properties were in reasonable agreement with experiment, the atomic charges bore little relation to reality. Thus the hydrogen atoms in paraffins were predicted to carry charges of ca. 0.5 e⁻. The errors were due to the parametrization having become trapped in an unsatisfactory minimum on the parameter hypersurface.

(13) Zoebisch, E. G. Ph.D. Dissertation, The University of Texas at Austin, 1987.

(14) Dewar, M. J. S.; Hashmall, J. A.; Venier, C. G. *J. Am. Chem. Soc.* **1968**, *90*, 1953.

**Table III. Mean Unsigned Errors in Heats of Formation[a] Calculated by AM1 for Various Types of Compounds Containing Aluminum**

| class | no. of examples | mean unsigned error |
|---|---|---|
| all species | 50 | 12.39 |
| neutral, closed shell | 27 | 10.73 |
| neutral, radical | 6 | 8.57 |
| ionic, closed shell | 11 | 15.07 |
| ionic, radical | 6 | 18.74 |
| all closed shell | 33 | 11.99 |
| all radicals | 17 | 13.66 |
| oxygen-containing compounds | 17 | 17.37 |
| halogen-containing compounds | 27 | 12.98 |
| organoaluminum compounds | 3 | 7.69 |

[a] Units: kcal/mol.

**Table IV. Calculated and Observed Dipole Moments[a]**

| | dipole moment[a] | | error in calcd dipole moment | | |
|---|---|---|---|---|---|
| species | exptl | AM1 | AM1 | MNDO | PM3 |
| AlCl[b] | 1.5 | 0.9 | −0.6 | 1.0 | 0.0 |
| AlF[c] | 1.53 | 1.0 | −0.5 | −1.2 | 0.2 |
| AlH[d] | 0.17 | 1.0 | 0.8 | −0.1 | 0.5 |
| mean unsigned error | | | 0.63 | 0.77 | 0.23 |

[a] Units: Debye. [b] Lide, D. *J. Chem. Phys.* **1965**, *42*, 1013. [c] Lavas, F. J.; Tiemann, E. *J. Phys. Chem. Ref. Data* **1974**, *3*, 609. [d] Cade, P. E.; Huo, W. M. *J. Chem. Phys.* **1966**, *45*, 1063.

**Table V. Calculated and Observed Ionization Potentials[a] (IP)**

| | IP[a] | | error in calcd IP | | |
|---|---|---|---|---|---|
| species | exptl | AM1 | AM1 | MNDO | PM3 |
| $Al_2$[b] | 5.8 | 6.3 | 0.5 | −0.2 | 0.5 |
| $AlBr_3$[c] | 10.91 | 11.5 | −0.6 | 1.1 | 3.4 |
| AlCl[d] | 8.5 | 8.8 | 0.3 | 0.1 | 0.6 |
| $AlCl_3$[c] | 12.01 | 12.5 | 0.5 | 1.1 | −0.6 |
| AlF[e] | 9.80 | 8.9 | −0.9 | −1.2 | −0.5 |
| $AlF_3$[f] | 16.10 | 13.8 | −2.3 | −1.5 | −0.9 |
| $AlI_3$[c] | 9.66 | 10.9 | 1.3 | 1.3 | 1.2 |
| AlClO[g] | 12.00 | 11.6 | −0.4 | −0.3 | −1.0 |
| AlH[h] | 8.40 | 8.0 | −0.4 | −0.7 | 1.3 |
| AlOH[i] | 7.50 | 8.7 | 1.2 | 0.5 | 1.6 |
| $Al(CH_3)_3$[c] | 9.76 | 10.3 | 0.6 | 0.9 | −0.4 |
| mean unsigned error | | | 0.82 | 0.81 | 1.09 |

[a] Units: electronvolt. [b] Hanley, L.; Rualta, S. A.; Anderson, S. L. *J. Chem. Phys.* **1980**, *87*, 260. [c] Barker, G. K.; Lappert, M. F.; Pedley, J. B.; Sharp, G. J.; Westwood, N. P. C. *J. Chem. Soc., Dalton Trans.* **1975**, 1765. [d] Berkowicz, J.; Dehmer, J. L. *J. Chem. Phys.* **1972**, *57*, 3194. [e] Singh, M. *Astrophys. Space Sci.* **1988**, *140*, 421. [f] Dyke, J. M.; Kirby, C.; Morris, A.; Gravenor, B. W. F.; Klein, R.; Rosmus, P. *J. Chem. Phys.* **1984**, *88*, 289. [g] Levin, R. D.; Lias, S. G. *Ionization Potentials and Appearance Potential Measurements, 1971–1981*; National Standard Reference Data Service, National Bureau of Standards, 1982; 71. [h] Rosmus, P.; Meyer, W. *J. Chem. Phys.* **1977**, *66*, 13. [i] Farber, M.; Frisch, M. A.; Grenier, G.; Ko, H. C. Space Sciences, Inc., Final Report, USAF Contract F04 611-67-C-00100, AFRPL-TR-67-144, No. 1967.

**Table VI. Calculated and Observed Geometries for Compounds Containing Aluminum**

| molecule | geometric values[a] | ref |
|---|---|---|
| $Al_2$ | Al–Al, 2.50 (2.47) | *b* |
| AlBr | Al–Br, 2.27 (2.30) | *b* |
| $Al_2Br_6$ | Al–Br, 2.21 (2.22); Al–Br (bridge), 2.37 (2.41) | *b* |
| AlCl | Al–Cl, 1.83 (2.13) | *b* |
| $AlCl_3$ | Al–Cl, 1.83 (2.06); ClAlCl, 120.0 (118) | *b* |
| $Al_2Cl_6$ | Al–Cl, 2.19 (2.06); Al–Cl (bridge), 2.05 (2.25) | *b* |
| AlF | Al–F, 1.54 (1.65) | *b* |
| $AlF_3$ | Al–F, 1.60 (1.63); FAlF, 120.0 (120.0) | *c* |
| $Al_2F_6$ | Al–F, 1.52 (1.63); Al–F (bridge), 1.75 (1.80) | *c* |
| $AlI_3$ | Al–I, 2.39 (2.50); IAlI, 120.0 (120.0) | *b* |
| $Al_2I_6$ | Al–I, 2.40 (2.45), Al–I (bridge), 2.51 (2.63) | *b* |
| AlH | Al–H, 1.47 (1.65) | *d* |
| AlN | Al–N, 1.42 (1.65) | *b* |
| $Al_2O$ | Al–O, 1.66 (1.73); AlOAl, 180.0 (180.0) | *b* |
| $Al(CH_3)_3$ | Al–C, (1.88); CAlC, 120.0 (120.0) | *e* |
| AlO | Al–O, 1.55 (1.62) | *b* |
| AlS | Al–S, 1.74 (2.03) | *f* |

[a] A–B, bond length (angstroms); ABC, bond angle (degrees). Observed values in parentheses. [b] Reference *a*, Table II. [c] Ashikin, P. A.; Rambidi, N. G.; Zasorin, E. Z. *Sov. Phys. Crystallogr.* **1959**, *4*, 167. [d] Bauschlicher, Jr., C. W.; Langhoff, S. R. *J. Chem. Phys.* **1988**, *89*, 2116. [e] Calloman, J. H.; Hirota, E.; Kuchitsu, K.; Lafferty, W. J.; Maki, A. G.; Pote, C. S. *Structure Data on Free Polyatomic Molecules*; Landolt-Bernstein, Hellwege, K. H.; Hellwege, A. M., Eds.; Springer: Berlin, 1976; New Series, Group II, Vol. 7. [f] Chase, Jr., M. W.; Davies, G. A.; Downey, Jr., J. R.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *JANAF Thermochemical Tables*, 3rd ed.; *J. Phys. Chem. Ref. Data, Suppl. 1* **1985**, *14*.

pulsion function, which in AM1 or PM3 contains additional Gaussian terms. Here only a single Gaussian proved necessary, in contrast to PM3, where two are included. Since each Gaussian term involves three independent parameters, the number of aluminum parameters is correspondingly less in AM1 than in PM3. A further difference lies in the treatment of the $\beta$ and $\zeta$ parameters for s and p AOs. These are allowed to vary from one another in AM1, whereas in MNDO they were set equal. As in MNDO, Oleari's values[15] were used for the one-center electron repulsion integrals, *g* and *h*.

Note the significant differences between the parameters in AM1 and PM3. These indeed correspond to different minima on the parameter hypersurface. As the results below show, our parameters lead to results that are significantly better than those given by PM3, indicating that Stewart's results failed to lead to the best minimum.

**Heats of Formation.** Table II compares the AM1 heats of formation ($\Delta H_f$) for a number of molecules with experiment and with the values given by MNDO and PM3. The AM1 results are generally better than those from either of the other procedures, and the mean unsigned error is also less for AM1; see the bottom of Table II.

The larger errors mostly refer to species where individual atoms carry large formal charges, e.g., ALFO, $AlO_2H$, $AlF_4^-$, $AlF_2O^-$, and $AlF^+$, molecules where the aluminum atom is predicted in each case to carry nearly a full unit of positive charge. The AM1 results are also less satisfactory for ions and radicals containing fluorine where the fluorine atoms tend to be highly charged. As expected on this basis, the errors for closed-shell fluorine compounds are much smaller than those for the ions. Table III compares the mean unsigned errors for various classes of compound.

**Dipole Moments and Ionization Potentials.** Table IV compares the calculated and observed dipole moments for three polar compounds of aluminum for which experimental values are available. While the PM3 values agree better with experiment than those from AM1, the compounds in question are hardly typical. The difficulty here is that most neutral aluminum compounds are nonpolar.

More data are available for ionization potentials of aluminum compounds. Table V compares the observed values with those given by MNDO, AM1, and PM3, the ionization potentials being derived from orbital energies by using Koopman's theorem.[16] While AM1 performs somewhat better than PM3, the errors are larger than with those for compounds of the first-row elements.[4]

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(15) Oleari, L.; Di Sipio, L.; De Michelis, G. *Mol. Phys.* **1966**, *10*, 97.

(16) Koopmans, T. *Physica* **1034**, *1*, 104.

**Geometries.** Table VI compares the calculated (AM1) geometries with experiment. The mean unsigned error in bond lengths is 0.12 Å, and the signed error −0.10 Å. The calculated aluminum bond lengths are thus systematically too short, a tendency already noted in AM1.[4] AM1, like MNDO,[7] predicts the linear (Al–O–Al–O) forms of both $Al_2O_2$ and $Al_2O_2^+$ to be more stable than the previously assumed square-planar structures, while AlOH is predicted to be linear rather than bent. Further studies of these molecules would be of interest.

**Conclusions.** We have produced a useful set of AM1 parameters for aluminum. The results from calculations using our values are generally closer to experimental than either MNDO or Stewart's newly introduced PM3.

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# Isolation and Crystal Structure of a Presumed Intermediate in the Reaction of an Organolithium Compound with an Epoxide

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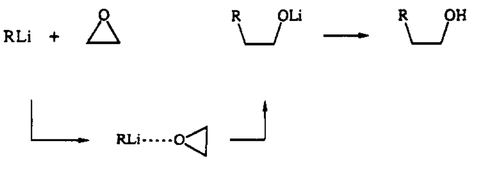
The organolithium–epoxide complexes tetrakis(1-lithio-2-methoxybenzene)–bis(ethylene oxide) and tetrakis(1-lithio-2-methoxybenzene)–bis(propylene oxide), which are thought to be intermediates in the β-hydroxyalkylation of organolithium compounds, have been isolated and characterized. NMR studies on these complexes in nonpolar solvents such as benzene and toluene provide evidence for epoxide oxygen to lithium coordination. Additionally, the propylene oxide complex has been characterized by single-crystal X-ray diffraction at 100 K. The compound crystallizes in the triclinic system (space group $P\bar{1}$) with chemical formula $4[C_7H_7OLi]\cdot 2[C_3H_6O]$ and $Z = 2$. Cell dimensions: $a = 11.348$ (1) Å, $b = 12.043$ (1) Å, $c = 12.099$ (1) Å, $\alpha = 95.57$ (1)°, $\beta = 92.30$ (1)°, $\gamma = 97.52$ (1)°. The structure consists of a tetrameric aggregate of 1-lithio-2-methoxybenzene and two disordered propylene oxide molecules, which coordinate to lithium as external Lewis bases. Since ab initio calculations (RHF; SV 3-21G) show the activation of the epoxide by lithium coordination to be very small, the question of whether such complexes are intermediates in the nucleophilic ring opening of epoxides remains unanswered.

## Introduction

The introduction of a β-hydroxyalkyl group by reaction of a nucleophilic species with an epoxide is an important synthetic operation. Depending upon the nature of the nucleophile and the structure of the epoxide, this reaction is carried out in different solvent systems[1] (eq 1 and 2).



(1)

(2)

This nucleophilic ring opening of epoxides is assumed to be facilitated by electrophilic assistance by acids, protic solvents, or Lewis acids.[2,3] It was found that the acid-catalyzed ring opening of ethylene oxide (EO) proceeds via the protonated species.[3,4] Ab initio calculations[4] (STO-5G) have shown this oxonium cation to be activated toward nucleophilic ring opening since (i) its C–O bond is elongated (and presumably weakened) compared to that in EO and (ii) the calculated electron density on the carbon atoms of EO decreases upon protonation.

In analogy with the acid-catalyzed ring opening, it is generally assumed that the reaction of an epoxide with an organolithium compound in solvents such as diethyl ether and tetrahydrofuran (THF) is assisted by coordination of the epoxide toward lithium.[5] This assumption seems

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