Molecular Mechanics. The MM3 Force Field for Hydrocarbons. 3. The van der Waals' Potentials and Crystal Data for Aliphatic and Aromatic Hydrocarbons[‡]

Jenn-Huei Lii and Norman L. Allinger*

Contribution from the School of Chemical Sciences, Department of Chemistry, University of Georgia, Athens, Georgia 30602. Received March 2, 1989

Abstract: The van der Waals' potentials used for interactions between carbon and hydrogen in both aliphatic and aromatic systems have been improved from those available in MM2, and the new values are used in MM3. The atoms are slightly larger and somewhat softer than they were with MM2. These values were optimized by fitting to the crystal parameters (six cell constants) and the heats of sublimation for the normal alkanes from C_6 to C_{10}, plus C_{12}, and also diamond, graphite, benzene, biphenyl, and hexamethylbenzene, in addition to fitting structural and energy data on congested molecules as reported earlier. The parameters developed give good crystal structures and heats of sublimation for these molecules. Biphenyl is calculated to be twisted about 40° in the gas phase, but lattice forces cause it to flatten into a planar conformation in the crystal.

For many simple organic molecules, since there is not very much stretching, bending, or torsional deformation, the most important quantities for determining their molecular structures are the nonbonded interactions. For nonpolar hydrocarbons, the only nonbonded interactions are the van der Waals' interactions among carbons and hydrocarbons in our formalism, and for most other organic compounds, the bulk of these interactions are still among these atoms. Therefore, the selection of adequate van der Waals' functions for these atoms is very important in molecular mechanics calculations.

Various sets of van der Waals' functions have been used by earlier workers for different calculations.[1] For the most part, the functions used were adequate for the purpose of which they were intended. The selection of a function which represents the van der Waals' interactions between nonbonded atoms (excluding 1,3 interactions) poses a problem, for there is no direct way to experimentally determine such a function. Hill has shown that the van der Waals' functions for the rare gas atoms and a few simple molecules can be expressed in terms of a reduced function involving two parameters for each atom;[2] one is the van der Waals' radius of the atom, and the other is an energy scale factor which measures the depth of van der Waals' energy well. Since Hill's function seemed to be as good as any available, we used it for early force fields.[3] In the MM2 force field,[4] a modified Hill's potential was used, because the earlier MM1 force field[5] had shown that the original function was too hard.

The van der Waals' potential used in the MM2 force field fit fairly well to the then available information, but it has subsequently turned out that the function for hydrogen–hydrogen interactions was still too hard for some very crowded systems. For example, the closest H/H distance in *exo,exo*-tetracyclo[6.2.1.1^{3,6}.0^{2,7}]-dodecane was calculated to be much too large (1.89 versus 1.75 Å experimentally).[6] Therefore, an important initial goal of this work was to find an adequate function which would represent the van der Waals' interactions between carbons and hydrogens.

Since our molecular mechanics calculations assume that intramolecular and intermolecular nonbonded interactions follow the same laws and use the same parameters, and the lattice forces which determine the crystal spacings and energy are just the van der Waals' forces (for the case of neutral nonpolar molecular crystals), the crystal structures of molecular substances may be used to calibrate nonbonded potential parameters.[3] In this work we established, in part using least-squares criteria, the sets of van der Waals' parameters for aliphatic and aromatic hydrocarbon compounds that would give the best fit of the crystallographic data and the heats of sublimation of several simple compounds (the *n*-alkanes from hexane to decane plus dodecane and benzene,

biphenyl, and hexamethylbenzene), and also give good molecular structures and other properties.[7,8]

Basis and Computational Method

Basis. It is well known that when the energy difference between the ground and lowest excited electronic states of a molecule is more than about 1.0 eV (which is almost always the case in organic crystals, since they are quite perfect dielectrics), one can make use of the so-called adiabatic approximation[9] which permits the reduction of the Coulombic interactions between nuclei and electrons to the interactions of atoms. In this case, the potential energy of atomic interaction, which merely depends on the coordinates of nuclei ("centers" of atoms), appears to be equal to the energy of the ground electronic level. The free energy, G, of a molecule is then given by

$$G \approx V_{r_{ij}} + K + PV - TS \tag{1}$$

where $V_{r_{ij}}$ is the equilibrium value of the potential energy, K is the kinetic energy (including zero-point vibrational energy and thermal energies), PV is the product of the pressure and volume, S is the entropy, and T is the absolute temperature. In the case of crystals, we can go somewhat further if we subdivide the free energy into two parts, inter- and intramolecular terms

$$G_{\text{crystal}} = E_{\text{inter}} + E_{\text{intra}} + PV - T(S_{\text{inter}} + S_{\text{intra}}) \tag{2}$$

where internal energies E_{inter} and E_{intra} are defined as

$$E_{\text{inter}} = V_{\text{inter}}(r_{ij}) + K_{\text{inter}} \tag{3}$$

$$E_{\text{intra}} = V_{\text{intra}}(r_{ij}) + K_{\text{intra}} \tag{4}$$

We made two main assumptions in our calculations: first, the molecule has a rigid conformation in the crystal (in other words, the deformation of molecule by the crystal packing forces is negligible);[10] second, the zero-point and thermal energies and the entropy contributed from the crystal lattice vibrations are assumed to be constant.[11] Under the first assumption, the intramolecular

---

(1) Burkert, U.; Allinger, N. L. In *Molecular Mechanics*; American Chemical Society: Washington, DC, 1982.
(2) Hill, T. L. *J. Chem. Phys.* **1948**, *16*, 399.
(3) Allinger, N. L.; Miller, M. A.; van Catledge, F. A.; Hirsch, J. A. *J. Am. Chem. Soc.* **1967**, *89*, 4345.
(4) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127.
(5) Wertz, D. H.; Allinger, N. L. *Tetrahedron* **1974**, *30*, 1579.
(6) Ermer, O.; Mason, S. A. *J. Chem. Soc., Chem. Commun.* **1983**, *1*, 53.
(7) Paper 1: Allinger, N. L.; Yuh, Y. H.; Lii, J.-H. *J. Am. Chem. Soc.*, accompanying paper in this issue.
(8) Paper 2; Lii, J.-H.; Allinger, N. L. *J. Am. Chem. Soc.*, accompanying paper in this issue.
(9) Leibried, G. In *Handbuch der Physik*, Band VII, Teil 2; Springer: Berlin, 1955.
(10) Warshel, A.; Lifson, S. *J. Chem. Phys.* **1970**, *53*, 582.
(11) To simplify the calculation, we neglected the effect of crystal packing forces on the thermal vibrational motions.

© 1989 American Chemical Society

MM3 Force Field for Hydrocarbons

J. Am. Chem. Soc., Vol. 111, No. 23, 1989 8577

Table I. van der Waals' Parameters for Saturated Hydrocarbons

interaction	MM2[a]	MM3[b]
C/C	3.80/0.0440[c]	4.08/0.0270
H/H	3.00/0.0470	3.24/0.0200
C/H	3.34/0.0460	3.56/0.0230
H offset	0.915	0.923

[a] MM2: $E_{vdw} = \epsilon(290\,000 \exp(-12.5d/D) - 2.25(D/d)^6)$. [b] MM3: $E_{vdw} = \epsilon(184\,000 \exp(-12.0d/D) - 2.25(D/d)^6)$. [c] D/ϵ: van der Waals' distance (Å)/energy scale factor (kcal/mol).

internal energy and entropy become constant, while, under the second assumption, the intermolecular kinetic energy and entropy terms are also regarded as constants. The intermolecular potential energy at equilibrium is dependent on the arrangement of the centers of mass of the molecules R_i, as well as on the molecular orientations as determined by the Eulerian angles θ_k,[12] since the PV term is so small compared to the intermolecular potential energy that it can be neglected in the calculation. Therefore, the total free energy of the crystal lattice becomes

$$G_{crystal} = V_{inter}(R_i, \theta_k) + \text{constant} \qquad (5)$$

The simplest assumption that can be made for studying the potential energy of intermolecular interactions is that of pairwise additivity.[13] Thus the intermolecular potential energy of the crystal may be represented as the sum over all pairs of nonbonded atoms of different molecules.

The major interatomic nonbonded potential function, the van der Waals' function, used in this work is represented by the (exp-6) function, and is assumed to be isotropic and temperature independent

$$E_{vdw} = \epsilon_{ij}[184\,000 \exp(-12.0d_{ij}/D_{ij}) - 2.25(D_{ij}/d_{ij})^6] \qquad (6)$$

where ϵ_{ij} is an energy scale factor for each atom pair which measures the interaction energy, D_{ij} is the van der Waals' distance, and d_{ij} is the effective distance between interacting centers of two atoms. Usually ϵ_{ij} is defined by $\sqrt{\epsilon_i}\sqrt{\epsilon_j}$ and D_{ij} represent the van der Waals' radii of the atoms. For the C/H interaction, there is a special treatment (discussed later). A comparison of the van der Waals' function of MM2[1,4] with that of MM3 (this work) is shown in Table I and in Figure 1. The MM3 van der Waals' potential is softer than that in MM2.

Computational Method. It is obvious that the packing of molecules in an observed crystal structure should correspond to a minimum point of total free energy of the crystal. In this work, using a given set of potential parameters, the location of the lattice energy minimum was found by a SIMPLEX procedure. This procedure involves calculation of the lattice energy with respect to the geometrical parameters, which will properly define the position of atoms in the unit cell and iteratively adjust the geometrical parameters in the direction of the best point until the minimum is found. Since the energy minimization involves iterative adjustment, the selection of a minimum number of geometrical parameters becomes important. As we assumed previously, the molecule itself has a rigid conformation in the crystal. Therefore, the positions of all of the atoms in the unit cell can be simply defined by the position of the centers of mass of the molecules and the Eulerian angles which define the positions of the intramolecular atoms relative to the center of mass of that molecule.

For the simplest crystal system (assuming only one rigid molecule in the crystallographic unit cell, and with the centers of mass of eight molecules placed at the corners of the cell), there are a total of 24 coordinates needed to define the positions of these mass centers in the unit cell. Twelve of them are fixed by the symmetry of the unit cell,[14] and the remaining 12 are the six unit cell parameters, three rotations and three translations. Since rotations and translations of the unit cell itself do not change the
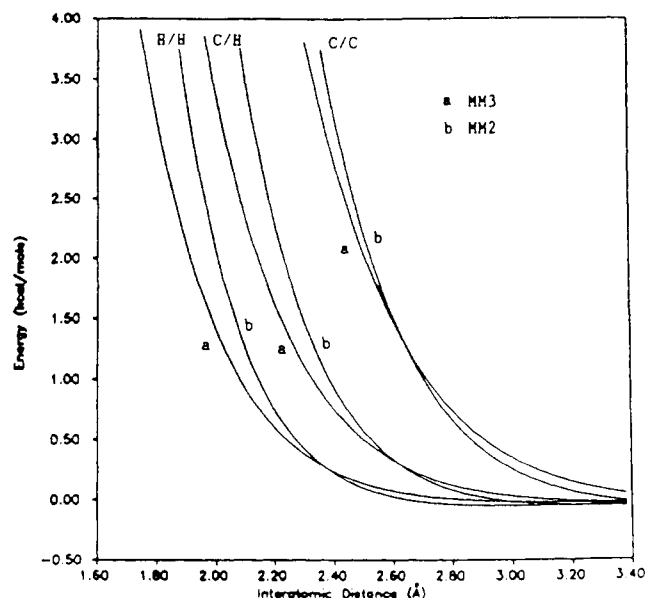

Figure 1. The van der Waals' potential curves of MM2 and MM3 for aliphatic C/C, C/H, H/H interactions. For interactions involving H, the distances are as shown when the C–H bonds are parallel to each other. If the approach is head on, the distances shown have to be lengthened by the factor of 0.077 times the sum of the C–H bond lengths (see text).

relative positions of mass centers of molecules, the six unit cell parameters become the only ones needed to define the positions of these centers. The smallest set of geometrical parameters, in this case, are the six unit cell parameters $(a, b, c, \alpha, \beta, \gamma)$ and the three Eulerian angles $(\theta_x, \theta_y, \theta_z)$. Of course, for a more complicated crystal system, such as the benzene crystal, more geometrical parameters must be introduced.

In practice it is necessary to impose a summation limit on the pairwise summation process. As the summation limit is increased, the number of terms in the lattice sum increases rapidly, but the energy contribution of each term becomes smaller and eventually has little effect on the unit cell parameters. A significant amount of lattice energy may be lost, however, by too low a summation limit. In earlier work it was found that by considering a block of 27 unit cells (3 × 3 × 3), the calculated crystal spacings of minimum lattice energy were in satisfactory agreement with experiment;[3] when the calculations were carried out on a 4 × 4 × 4 or 5 × 5 × 5 block of unit cells, these spacings were reduced by less than 0.01 Å, showing that the 3 × 3 × 3 crystal size is adequate for determining the crystal structure. From the interaction energy between two molecules at various distances along the a, b, c axes, the energy required to remove a single molecule from an infinite block of molecules was calculated, and this is related to the heat of sublimation of our idealized crystal.[15] The value found directly from this calculation was not the actual heat of sublimation; some further corrections are necessary to obtain a number that can be compared with experiment.[16]

In this work, a Fortran program CRSTL, using the MM2 or MM3 van der Waals' functions, was written for locating the lattice energy minimum of the crystal and calculating the heat of sublimation. The CRSTL program read in the molecular coordinates which had been previously optimized by MM2 or MM3, and the initial "guessed" values of the unit cell parameters $(a, b, c, \alpha, \beta, \gamma)$ and Eulerian angles $(\theta_x, \theta_y, \theta_z)$, as input.[17] The program then

(12) Goldstein, H. In *Classical Mechanics*; Addison-Wesley: Cambridge, MA, 1951.

(13) Westheimer, F. H. In *Steric Effects in Organic Chemistry*; Newman, M. S., Ed.; Wiley: New York, 1956, p 523.

(14) Williams, D. E. *J. Chem. Phys.* **1966**, *45*, 3770.

(15) A cubical block of 3375 unit cells was actually used, and the energy needed to pull out the middle molecule was calculated. The change in the calculated energy which would result if an infinite block was used is estimated greater than this value by less than 0.1 kcal/mol (ref 3).

(16) The value calculated directly from the intermolecular interaction is the lattice energy. A further correction, the amount of energy required to establish the conformational mixture which exists in the gas phase from the perfectly staggered arrangement which exists in the crystal, is needed to obtain the actual heat of sublimation.

Table II. Unit Cell Parameters and Heat of Sublimation for *n*-Hexane

parameters	MM2	MM3	exptl[19]	dev (%)[a]
a	4.17	4.34	4.17 ± 0.02	4.1
b	4.45	4.63	4.70 ± 0.02	-1.5
c	8.48	8.67	8.57 ± 0.02	1.2
α	95.3	96.2	96.6 ± 0.3	-0.4
β	88.0	89.8	87.2 ± 0.3	3.0
γ	103.1	103.6	105.0 ± 0.3	-1.3
vol	152.7	168.1	161.0	4.4
E_{sub}	19.31	11.59	9.76	18.7

[a] (MM3 − exptl).

Table III. Unit Cell Parameters and Heat of Sublimation for *n*-Octane

parameters	MM2	MM3	exptl[20]	dev (%)[a]
a	4.15	4.32	4.22 ± 0.02	2.4
b	4.44	4.63	4.79 ± 0.02	-3.3
c	10.99	11.13	11.02 ± 0.02	1.0
α	95.1	95.1	94.7 ± 0.3	0.4
β	84.6	86.0	84.3 ± 0.3	2.0
γ	102.4	103.0	105.8 ± 0.3	-2.6
vol	196.3	215.5	214.0	0.7
E_{sub}	25.77	15.91	15.13	5.2

[a] (MM3 − exptl).

Table IV. Unit Cell Parameters and Heat of Sublimation for *n*-Decane

parameters	MM2	MM3	exptl[21]	dev (%)[a]
a	4.16	4.34	4.20 ± 0.02	3.3
b	4.44	4.64	4.75 ± 0.02	-2.3
c	13.46	13.58	13.57 ± 0.02	0.1
α	93.6	94.1	93.4 ± 0.3	0.7
β	82.2	83.7	81.8 ± 0.3	2.3
γ	102.6	102.8	105.0 ± 0.3	-2.7
vol	240.4	264.1	258.0	2.4
E_{sub}	32.29	20.22	19.53	3.5

[a] (MM3 − exptl).

Table V. Unit Cell Parameters and Heat of Sublimation for *n*-Dodecane

parameters	MM2	MM3	exptl[21]	dev (%)[a]
a	4.16	4.34	4.28 ± 0.02	1.4
b	4.44	4.64	4.81 ± 0.02	-3.5
c	15.98	16.08	16.12 ± 0.02	-0.2
α	93.3	93.3	93.3 ± 0.3	0.0
β	80.5	81.8	79.9 ± 0.3	2.4
γ	102.8	102.8	106.6 ± 0.3	-3.6
vol	283.8	312.0	313.0	-0.3
E_{sub}	38.77	24.52	23.78	3.1

[a] (MM3 − exptl).

Table VI. Unit Cell Parameters and Heat of Sublimation for *n*-Heptane

parameters	MM2	MM3	exptl[22]	dev (%)[a]
a	4.14	4.34	4.15 ± 0.01	4.6
b	4.44	4.65	4.69 ± 0.01	-0.9
c	20.12	20.23	19.97 ± 0.02	1.3
α	91.6	91.4	91.3 ± 0.2	0.1
β	94.3	93.5	94.9 ± 0.2	-1.5
γ	102.9	103.7	105.7 ± 0.2	-1.9
vol	359.4	395.6	373.0	6.1
E_{sub}	22.01	13.45	12.60	6.7

[a] (MM3 − exptl).

Table VII. Unit Cell Parameters and Heat of Sublimation for *n*-Nonane

parameters	MM2	MM3	exptl[21]	dev (%)[a]
a	4.15	4.33	4.13 ± 0.01	4.8
b	4.44	4.64	4.70 ± 0.01	-1.3
c	25.03	25.24	24.92 ± 0.02	1.3
α	91.2	91.2	92.9 ± 0.2	-1.8
β	97.1	95.9	91.9 ± 0.2	4.4
γ	102.7	102.7	105.2 ± 0.2	-2.4
vol	446.1	491.7	466.0	5.5
E_{sub}	28.49	17.76	16.19	9.7

[a] (MM3 − exptl).

constructed a block of 27 unit cells (3 × 3 × 3) as the starting crystal geometry according to this input formation, which was then optimized by iteratively adjusting the geometrical parameters until the lattice energy minimum was found. The program then printed out the optimized geometrical parameters, and also generated a block of 3375 unit cells (15 × 15 × 15) for plotting and calculation of the heat of sublimation.[16] The program flow chart for CRSTL is shown in Chart I.

Results and Discussion

Results. Beginning with simple normal aliphatic hydrocarbon molecules, we sought to derive van der Waals' parameters for the C/C, H/H, and C/H interactions. These parameters were determined to give what was judged to be the best possible agreement between the calculated properties and the corresponding available experimental data, such as molecular geometry, crystal unit cell parameters, and heat of sublimation.

I. Aliphatic Hydrocarbons. For the purposes of our calculation, we assumed that the normal aliphatic hydrocarbon molecules are rigid in the extended trans conformations, as indeed they are observed in the crystal. The geometries of these hydrocarbons which were used in the optimization of unit cell parameters were first refined by the MM2 or MM3 (this work) force field. Meanwhile, in order to account for the anisotropy of the non-bonded interactions (i.e., that interactions depend on the relative orientations of the interacting bond orbitals in a manner which cannot be fully represented as a sum of functions of interatomic distances), we, based on our calculations on hydrogen atom repulsion and attraction centers, located 92.3% of the calculated C–H bond length from the carbons.[1,4,18] We established the best set of van der Waals' parameters for the C/C, H/H, and C/H interactions. The values of these parameters are shown in the Table I. The potential curves for these interactions, defined in Table I, are shown in Figure 1.

For comparison, the experimental crystal structures of the aliphatic hydrocarbons were obtained from available X-ray crystallographic data,[19-22] and the heats of sublimation were

determined from the heats of vaporization and fusion published by Rossini et al.,[23] together with the integral of the heat capacity C_p evaluated graphically from measurements by Huffman et al.[24]

Calculation of the unit cell parameters and the heats of sublimation was carried out for *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane, and *n*-dodecane. It was found that van der Waals' parameters from this work give better crystal properties than did those from MM2. The heat of sublimation is improved quite a lot (compared to the MM2 force field), and the unit cell parameters are in reasonable agreement with experiment. But most important, these functions also lead to good molecular structures,[7] vibrational frequencies,[8] and other properties.[7,8]

***n*-Hexane, *n*-Octane, *n*-Decane, and *n*-Dodecane.** The crystal packing patterns of these four even-numbered *n*-paraffins are

(17) For more complicated crystal systems, such as *n*-heptane, *n*-nonane, and benzene, an additional seven geometrical parameters were introduced.
(18) Williams, D. E. *J. Chem. Phys.* **1965**, *43*, 4424.
(19) Norman, N.; Mathisen, H. *Acta Chem. Scand.* **1961**, *15*, 1755.
(20) Norman, N.; Mathisen, H. *Acta Chem. Scand.* **1967**, *21*, 127.
(21) Norman, N.; Mathisen, H. *Acta Chem. Scand.* **1972**, *26*, 3913.
(22) Merle, A. M.; Lamotte, M.; Risemberg, S. *Chem. Phys.* **1978**, *22*, 207.

(23) (a) Rossini, F. D., et al. *Natl. Bur. Std. (U.S.) Circ.*, **1947**, C461. (b) Rossini, F. D. In *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds*; Carnegie: Pittsburgh, PA, 1953.
(24) (a) Douslin, D. R.; Huffman, H. M. *J. Am. Chem. Soc.* **1946**, *68*, 1704. (b) Huffman, H. M.; Parks, G. S.; Barmore, M. *J. Am. Chem. Soc.* **1931**, *53*, 3876.
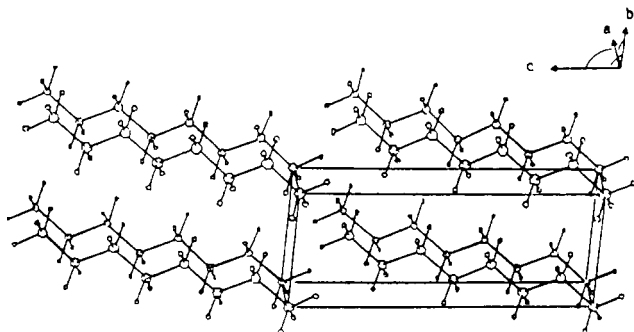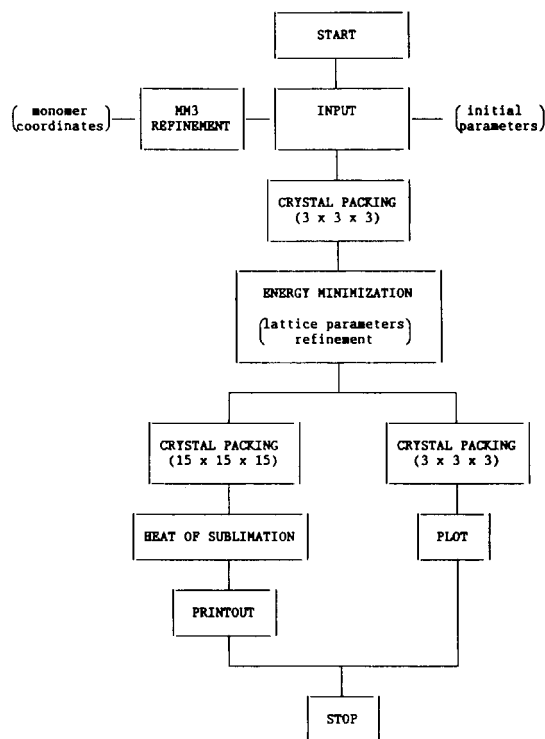
Figure 2. Calculated crystal packing of *n*-octane.

Chart I. Flow Diagram of CRSTL Program

Figure 3. Calculated crystal packing of *n*-heptane.

Table VIII. van der Waals' Parameters for Unsaturated Hydrocarbons

type of interaction	force fields	
	MM2[a]	MM3[b]
C/C	3.88/0.0440[c]	3.92/0.0560
H/H	3.00/0.0470	3.24/0.0200
C/H	3.44/0.0455	3.58/0.0335
H offset	0.915	0.923

[a] MM2: $E_{vdw} = \epsilon(290\,000 \exp(-12.5d/D) - 2.25(D/d)^6)$. [b] MM3: $E_{vdw} = \epsilon(184\,000 \exp(-12.0d/D) - 2.25(D/d)^6)$. [c] D/ϵ: van der Waals' distance (Å)/energy scale factor (kcal/mol).

Table IX. Benzene Dimerization Potential from MM2, MM3, and Other Calculations

methods	parallel[b]	perpendicular
ab initio[35,d]	−0.55/3.75	−2.59/4.89
Evans[a]	−2.54/3.44	−3.06/4.87
MM2	−4.13/3.46	−1.41/5.53
MM3*[c]	−3.49/3.54	−1.68/5.12
MM3	−1.82/3.69	−2.16/5.07

[a] The semiempirical potential was derived by fitting the second virial coefficient of benzene vapor (ref 36). [b] Potential energy (kcal/mol)/ mass center distance (Å) at the energy minimum point. [c] MM3 force field without dipole/dipole interaction. [d] The basis set used was approximately 6-31G** MP2.

similar and are triclinic with one molecule in the unit cell.[19-21] Each of these molecules has a crystallographic center of symmetry, and the chains pack in a parallel fashion with the unit cell parameters shown in the Tables II–V, respectively (Figure 2). In one column of each table, the unit cell parameters and heats of sublimation are given as calculated by using the MM2 force field and, in the next column, the corresponding values obtained using the MM3 force field. The "experimental values" for these quantities are given and also for the crystal volume. Note that the experimental crystal volumes were determined at low temperature; the MM2/MM3 values are for room temperature and should be slightly larger. Also note that the "experimental" heats of sublimation require extrapolations from the actual (low) temperatures to room temperature, and hence contain some uncertainty, especially in the case of hexane where the extrapolation is over a long temperature range.

n-Heptane and n-Nonane. *n*-Heptane[22] and *n*-nonane[21] have the same crystal packing, i.e., a triclinic cell containing two molecules. These two hydrocarbons have a C_{2v} symmetry, and two kinds of differently oriented chains are packed in parallel fashion with the unit cell parameters shown in Tables VI and VII, respectively (Figure 3). Again, the results indicate that MM3 is better than MM2.

II. Aromatics. Since there are differences in properties between aromatic and aliphatic hydrocarbons, we treat the aromatic and saturated carbons as different types of atoms in molecular mechanics calculations. We began with the graphite crystal, which
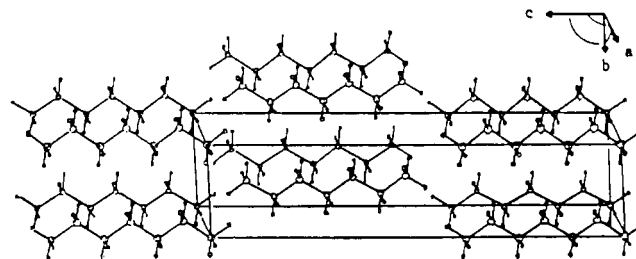
presents large van der Waals' interactions without the interference of other potential functions, and we determined the van der Waals' parameters for the C/C interaction by the method described by Sprague[25] to fit the experimental interplanar spacing and compressibility of the graphite crystal.[26] The parameters for H/H and C/H interactions were then derived from the crystal structures and properties of simple aromatic hydrocarbons, such as benzene,[27] biphenyl,[28] and hexamethylbenzene.[29]

The intermolecular potentials of aromatic crystalline hydrocarbons are more complicated than those in alkane crystals, because of π-electron interactions. Over the past few years, a number of workers have attempted to rationalize the structure of aromatic crystalline hydrocarbons by examining the various contributions to the intermolecular potentials,[14,30] and the intermolecular potential between two benzene molecules has been of fundamental interest for discussions of structure and energy transfer in condensed phases of aromatic systems. Although the actual most stable benzene dimer geometry is still uncertain, all recent experiments and calculations indicate that benzene dimers have two possible geometries, in one the rings are perpendicular and in the other, parallel.[31]

(25) Sprague, J. T.; Allinger, N. L. *J. Comput. Chem.* **1980**, *1*, 257.
(26) The MM3 force field calculates the following for graphite: interplanar spacing, 3.373 Å (exptl 3.354 Å); compressibility 2.84 × 10⁻¹² cm²/dyn (exptl 2.97 × 10⁻¹² cm²/dyn), and energy 2.6 kcal/mol (exptl 2.2 kcal/mol).
(27) Cox, E. G.; Cruickshank, D. W. J.; Smith, J. A. S. *Proc. R. Soc. London* **1958**, *A247*, 1.
(28) Charbonneau, G. P.; Delugeard, Y. *Acta Crystallogr.* **1976**, *B32*, 1420.
(29) Brockway, L. O. *J. Chem. Soc.* **1939**, 1324.
(30) (a) Rae, A. J. M.; Mason, R. *Proc. R. Soc. London* **1968**, *A304*, 487. (b) Banerjee, K.; Salem, L. *Mol. Phys.* **1966**, *11*, 405. (c) Craig, D. P.; Mason, R.; Pauling, P.; Santry, D. P. *Proc. R. Soc. London* **1965**, *A286*, 98.

Table X. Unit Cell Parameters and Heat of Sublimation for Benzene

parameters	MM2	MM3	exptl[27]	dev (%)[a]
a	6.75	7.07	7.03 ± 0.02	0.6
b	7.14	7.18	7.46 ± 0.02	-3.8
c	9.52	9.82	9.67 ± 0.02	1.6
α	89.6	85.5	90.0 ± 0.3	-5.0
β	90.8	90.7	90.0 ± 0.3	0.8
γ	89.3	90.1	90.0 ± 0.3	0.1
vol	459.0	493.2	507.1	-2.7
E_{sub}	11.18	10.32	10.42[39]	-0.1

[a](MM3 − exptl).

Table XI. Unit Cell Parameters and Heat of Sublimation for Biphenyl

parameters	MM2	MM3	exptl[28]	dev (%)[a]
a	7.74	7.79	7.82 ± 0.02	-0.4
b	5.48	5.60	5.58 ± 0.01	0.4
c	9.31	9.34	9.44 ± 0.02	-1.1
α	90.0	89.3	90.0 ± 0.0	-0.8
β	93.8	93.1	94.62 ± 0.10	-1.6
γ	89.6	88.9	90.0 ± 0.0	-1.2
vol	394.0	406.7	410.6	-0.9
E_{sub}	19.19	18.26	19.50 ± 0.5[40]	-6.4

[a](MM3 − exptl).

Starting with the investigation of benzene dimers, assuming the monomeric molecules are rigid, and offsetting the center of the van der Waals' interaction of hydrogen into the C–H bond by 7.7% of the bond length, we found that van der Waals' interactions alone cannot explain the perpendicular geometry properly, and (as suggested earlier by Williams[14]) electrostatic interactions must be taken into account. By choosing a bond dipole moment of 0.6 D for the $C(sp^2)$–H bond as suggested by Petro,[32] and including the dipole/dipole interaction in the calculation of benzene dimerization, we found that the results were in better agreement with experiment.[33] The selection of the best set of van der Waals's parameters for the unsaturated C/C, C/H, and H/H interactions was based on the calculations of benzene dimerization, and the structures of graphite and aromatic crystalline hydrocarbons. The values for these parameters and the potential curves for these interactions are shown in Table VIII; the comparison of calculated and semiempirical results for benzene dimerization potentials are shown in Table IX. Note that the parameters for aromatic carbon are a little different from those for aliphatic carbon.

Calculations of the unit cell parameters and the heat of sublimation were carried out for benzene, biphenyl, and hexamethylbenzene. The geometrical fits for the aromatic crystal structures were generally good, and heats of sublimation were also in good agreement with the experimental values.

1. Benzene. An idealized benzene molecule of D_{6h} symmetry and C–C distance of 1.397 Å was fit to the crystal structure[27] observed at −3 °C. The crystal structure is orthorhombic with four molecules in the unit cell. The molecule has a crystallographic center of symmetry, and the two closest molecules pack in a perpendicular fashion with the unit cell parameters shown in the Table X (see Figure 3 in ref 37).

(31) (a) Janda, K. C.; Hemminger, J. C.; Winn, J. S.; Novick, S. E.; Harris, S. J.; Klemperer, W. *J. Chem. Phys.* **1975**, *63*, 1419. (b) Steed, J. M.; Dixon, T. A.; Klemperer, W. *J. Chem. Phys.* **1979**, *70*, 4940. (c) Langridge-Smith, P. R. R.; Brumbaugh, D. V.; Haynam, C. A.; Levy, D. H. *J. Phys. Chem.* **1981**, *85*, 3742. (d) Hopkins, J. B.; Powers, D. E.; Smalley, R. E. *J. Phys. Chem.* **1981**, *85*, 3739. (e) Law, K. S.; Schauer, M.; Bernstein, E. R. *J. Chem. Phys.* **1984**, *81*, 4871.

(32) Petro, A. J. *J. Am. Chem. Soc.* **1958**, *80*, 4230.

(33) The MM2 and MM3* (without considering dipole/dipole interactions) force fields predicted the parallel geometry to be more stable, far beyond the observation, but the MM3 force field, with dipole/dipole interaction, gives a more reasonable result (see Table IX). MM2, with added charges, also gives good results for the benzene–benzene interaction (ref 34).

(34) Pettersson, I.; Liljefors, T. *J. Comput. Chem.* **1987**, *8*, 1139.

(35) Karlstrom, G.; Linse, P.; Walqvist, A.; Joensson, B. *J. Am. Chem. Soc.* **1983**, *105*, 3777.

(36) Evans, D. J.; Watts, R. O. *Mol. Phys.* **1976**, *31*, 83.

(37) Allinger, N. L.; Lii, J.-H. *J. Comput. Chem.* **1987**, *8*, 1146.
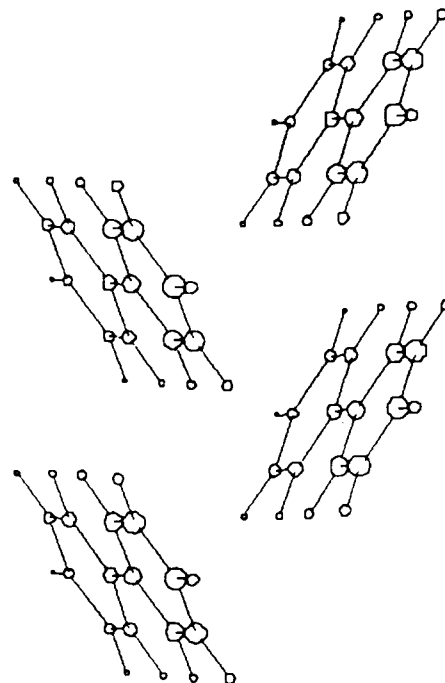
Figure 4. Calculated crystal packing of biphenyl.
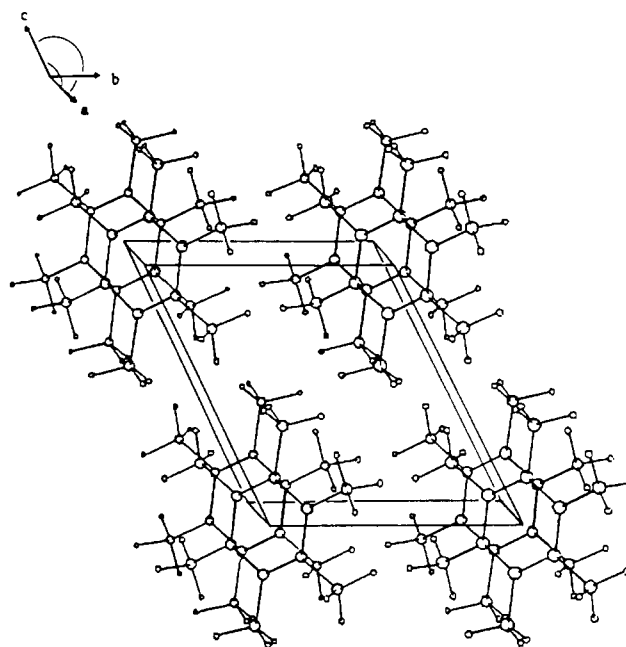
Figure 5. Calculated crystal packing of hexamethylbenzene.

Table XII. Unit Cell Parameters and Heat of Sublimation for Hexamethylbenzene

parameters	MM2	MM3	exptl[29]	dev (%)[a]
a	5.06	5.26	5.30 ± 0.02	-0.8
b	8.78	8.93	8.86 ± 0.02	0.8
c	8.81	8.97	8.92 ± 0.02	0.6
α	119.8	119.9	119.3 ± 0.0	0.5
β	116.3	116.2	116.4 ± 0.0	-0.2
γ	46.7	46.0	44.3 ± 0.0	3.8
vol	221.5	235.8	228.5	3.2
E_{sub}	24.81	16.83	17.86 ± 0.5[41]	-5.8

[a](MM3 − exptl).

2. Biphenyl. A coplanar biphenyl molecule refined by MM2 or MM3 was used in the calculation. The bond dipole moments for the C–H bonds are the same as those in the benzene molecule. The crystal packing is monoclinic with two molecules in the unit

MM3 Force Field for Hydrocarbons

J. Am. Chem. Soc., Vol. 111, No. 23, 1989 8581

Table XIII. Comparison of Calculated and Experimental Molecular Geometries of *n*-Octane

geometrical parameters	MM3[a]	exptl[20]
av C-C	1.54	1.53 ± 0.01
av C-C-C	112.4	112.0 ± 0.5
av H-C-H	107.1	111.0 ± 5.0
av C--C (1,3)[b]	2.55	2.54 ± 0.01

[a] All values are in angstroms (Å) and degrees. [b] The mean value of repeat distance along the molecular chain.

cell. The molecules pack in both perpendicular and parallel fashions with the unit cell parameters shown in Table XI (Figure 4).
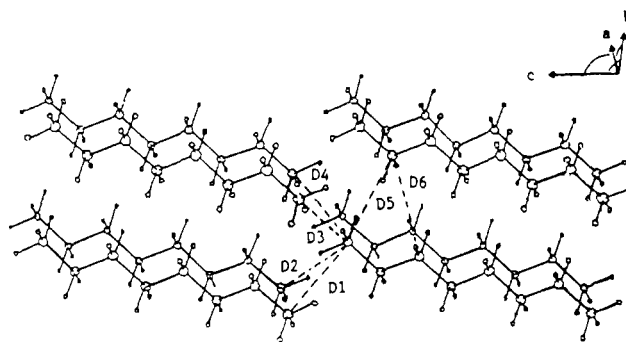
3. Hexamethylbenzene. A MM2 or MM3 refined hexamethylbenzene molecule with bond dipole moments of 0.9 D for the C(sp²)-C(sp³) bonds was used to calculate the crystal structure.[38] The crystal packing of hexamethylbenzene is triclinic with one molecule in the unit cell. All rings pack in a parallel fashion with the unit cell parameters shown in Table XII (Figure 5).

Discussion

Generally speaking, the fits of the crystal structures and heats of sublimation for both aliphatic and aromatic crystalline hydrocarbons obtained with MM3 in this work were good, even though the deviations were significant in some cases. One reason for such deviations could be the neglect of the vibrational contributions, as well as the under-estimation of the anisotropic character of nonbonded interactions in the crystal structure calculations. Several authors[42] have discussed the possible existence of strongly anisotropic electronic polarizabilities in molecules. It is well known that the molecular polarizability cannot be successfully resolved into atomic components.[43] This is physically reasonable, since the electrons in the bonding regions are loosely bound relative to the electrons close to the nucleus, and are therefore more polarizable.

The root-mean-square (rms) error of fit for the aliphatic heats of sublimation (excluding *n*-hexane[44]) was 6.1%, with a maximum of 9.7% for *n*-nonane. The errors in the calculated heats of sublimation were 0.1% for benzene, 6.4% for biphenyl, and 5.8% for hexamethylbenzene. The rms errors of the geometrical fits (for the six unit cell parameters) were 2.4% for the aliphatic hydrocarbons and 1.9% for the aromatics. The parameters chosen for the unsaturated nonbonded interactions gave slightly better fits to experiment than those for the saturated ones. A possible explanation is that the derivation of the unsaturated parameters was based on a better starting point, with the determination of C/C interactions by fitting the experimental data for the graphite crystal, which can be studied without interference from other functions.

Here are selected four typical crystalline hydrocarbons for further discussion: *n*-octane, *n*-heptane, benzene, and biphenyl. The crystal structure of *n*-octane has been well studied since 1930.[20,45] The calculated molecular geometry of *n*-octane (Figure 2) was in good agreement with the experiment as shown in Table XIII, and the molecules of this even numbered *n*-paraffin pack

(38) The bond dipole moment of 0.9 D for the C(sp²)-C(sp³) bond was chosen to reproduce the dipole moment of 0.3 D for toluene.

(39) The heats of sublimation were determined from the heats of vaporization and fusion, together with the integral of C_p evaluated graphically. See ref 23 and 24.

(40) Bradley, R. S.; Cleasby, T. G. *J. Chem. Soc.* **1953**, 1690.

(41) Frankosky, M.; Aston, J. G. *J. Phys. Chem.* **1965**, *69*, 3126.

(42) (a) London, F. *J. Phys. Chem.* **1942**, *46*, 305. (b) deBoer, J. *Physica* **1942**, *9*, 363. (c) Davies, P. L.; Coulson, C. A. *Trans. Faraday Soc.* **1952**, *48*, 777. (d) Davies, P. L. *Trans. Faraday Soc.* **1952**, *48*, 789.

(43) Denbigh, K. G. *Trans. Faraday Soc.* **1940**, *36*, 936.

(44) The reason we excluded *n*-hexane from the rms error calculation for the aliphatic heats of sublimation was because the value may not be reliable as the heat capacity function C_p must be extrapolated over such a long range.

(45) (a) Muller, A. *Proc. R. Soc. London* **1930**, *A127*, 417. (b) Norman, N.; Mathisen, H. *Acta Chem. Scand.* **1961**, *15*, 1747. (c) Norman, N.; Mathisen, H. *Acta. Chem. Scand.* **1964**, *18*, 353.

Figure 6. Closest contacts in the *n*-octane crystal.

Table XIV. Short Intermolecular Carbon-Carbon Distances in the *n*-Octane Crystal

vectors[a]	MM2	MM3	exptl[45b]	dev (%)[b]
D1	3.86	3.97	3.92	1.3
D2	4.25	4.40	4.33	1.6
D3	4.14	4.35	4.47	-2.7
D4	3.52	3.67	3.62	1.4
D5	3.79	3.97	4.11	-3.4
D6	3.84	4.01	4.14	-3.1

[a] The vectors are defined in Figure 6, and all values are in Å. [b] (MM3 - exptl).

in the extended trans conformation with one molecule in the unit cell (space group P1). The standard deviations between the calculated and observed shortest distances between carbon atoms of different molecules in the *n*-octane crystal were 1–3%, as shown in Table XIV and Figure 6.

Unlike the *n*-octane crystal, the crystal packing of *n*-heptane involves two differently oriented molecules[46] in the unit cell (space group P1̄), as shown in Figure 3. The calculated unit cell parameters were generally good. By carefully examining the calculated unit cell parameters of aliphatic hydrocarbons, we found that the calculated results are systematically 3.6% longer along the *a* axis, 2.3% shorter along the *b* axis, and 1.0% longer along the *c* axis. Some of this error may result from the fact that our crystal is so small. Some of the error is likely to arise from the anisotropic character of nonbonded interactions. In other words, the way to offset the effective interaction center, as well as the way we treat the effective nonbonded interactions as two-body interactions only, with spherical symmetry may not be good enough for representing the nonbonded interactions with greater accuracy than this. Further studies are necessary here.

The study of the benzene crystal structure was a most interesting and challenging task, because of the unusual crystal packing of benzene crystal. It has been established that the benzene crystal is orthorhombic, belonging to the space group *Pbca*, with four molecules in the unit cell. The molecules pack in both perpendicular and parallel fashions (shown in Figure 3, ref 37). The calculated results were rather good after including dipole/dipole interactions in the calculation. The 0.6 D value for the bond dipole moment for the C(sp²)-H bond fits the data not only for the benzene dimer and the benzene crystal, but also for the alkene energies and geometries.[47] The distance between mass centers of nearest neighbor benzene molecules in the crystal was calculated to be 5.05 Å (experimental value 5.00 Å[27]). The dihedral angle between the planes of molecules was calculated to be 81° (experimental value 84°[27]). The distances of the two closest hydrogen pairs were calculated to be 2.47 (exptl 2.64) and 3.11 (exptl 2.78).[27]

We examined another interesting case, biphenyl, with the same parameter set. It has been long known that the two benzene rings are not coplanar in this molecule in the gas phase. One is rotated to respect to the other by about 42°.[48] We calculated a torsional

(46) If the first *n*-heptane molecule has an "M" shape, then the second molecule is oriented in the "W" shape in the crystal.

(47) Li, F. Ph.D. Dissertation, University of Georgia, Aug 1987.

Table XV. Importance of Crystal Lattice Forces in Biphenyl Crystal

A. Energy of Conformations in the Isolated System

model	description	rel internal energy
1	X-ray (dihedral 0.0°)	1.98
2	hypo (dihedral 20.0°)	0.71
3	gas (dihedral 40.2°)	0.00

B. Energy of Conformations in the Crystal Lattice

model	internal energy[a]	lattice energy[b]	total energy[c]	heat of sublimation[d]
1	1.98	-20.28	-18.26	18.26
2	0.71	-17.65	-16.94	16.94
3	0.00	-15.64	-15.64	15.64

C. Comparison of Crystal Unit Cell Parameters of Conformations

parameters	model 1	model 2	model 3	exptl[28]
a	7.79	8.21	8.51	7.82 ± 0.02
b	5.60	5.78	6.03	5.58 ± 0.01
c	9.34	9.29	9.36	9.44 ± 0.02
α	89.3	87.8	84.1	90.0 ± 0.0
β	93.1	98.0	102.4	94.62 ± 0.10
γ	88.9	88.7	88.2	90.0 ± 0.0
vol	406.7	436.1	466.4	410.6
E_{sub}	18.26	16.94	15.64	19.5 ± 0.5[40]

[a] The internal energy is the difference in steric energy between the indicated conformation and the most stable conformation (model 3). [b] The lattice energy is the energy required to pull central molecule from the crystal lattice to an infinite distance. [c] The total energy of the crystal is taken to be the sum of internal energy and lattice energy. [d] The heat of sublimation (E_{sub}) is the difference between the internal energy of most stable isolated conformation (model 3) and the total energy of the appropriate crystal lattice.

angle of 40°, similar to that which was found with MM2. But it also has been long known that the biphenyl molecule is planar in the crystal.[28] The explanation ordinarily given is that crystal packing forces favor the planar over the nonplanar structure and hence force the molecule into a planar conformation. To understand this fact, we separately packed two rigid molecules, the

planar one, and the one which has the benzene rings rotated 40°, into crystal lattices made up of 27 unit cells and 54 molecules. We then optimized the lattice parameters, keeping the molecules rigid in each case. The internal molecular energy of an isolated biphenyl molecule increases about 1.98 kcal/mol in going from the twisted conformation to the planar one, but there was a stabilization of the planar crystal relative to the nonplanar one from the lattice forces by 4.64 kcal/mol, which easily outweighed the energy required to flatten the molecule. This information is summarized in Table XV.

Conclusions

van der Waals' parameters were derived to describe carbon and hydrogen in the MM3 force field that are significantly improved over those used in MM2. These new parameters adequately describe the crystals of the normal alkanes, both with respect to their structure and their heats of sublimation; they also describe a few simple aromatics, including graphite, benzene, and hexamethylbenzene. The long-standing problem of the conformation of biphenyl is resolved, with the demonstration that the lattice forces are sufficient to planarize the otherwise twisted molecule.

The van der Waals' function for hydrogen bound to carbon arrived at is in fairly good agreement with that postulated earlier by Bartell,[49] based on theoretical studies by Kochanski.[50] Since this work was completed, Wiberg has also published[51] van der Waals' functions for hydrogen–hydrogen interactions, based on ab initio calculations, and they are also quite similar to the MM3 function. The MM3 functions also work very well for intramolecular interactions (see papers 1[7] and 2[8]) at distances much shorter than the intermolecular distances found in crystals.

(48) (a) Bastiansen, O.; Traetteberg, M. *Tetrahedron* **1962**, *17*, 147. (b) Barrett, R. M.; Steele, D. *J. Mol. Struct.* **1972**, *11*, 105.

(49) Fitzwater, S.; Bartell, L. S. *J. Am. Chem. Soc.* **1976**, *98*, 5107.
(50) Kochanski, E. *J. Chem. Phys.* **1973**, *58*, 5823.
(51) Wiberg, K. B.; Murcko, M. A. *J. Comput. Chem.* **1987**, *8*, 1124.

Structural Investigations of Aluminum Cluster Ions, Al$_n^-$ (n = 3–50)

Robert L. Hettich

Contribution from the Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6120. Received November 18, 1988

Abstract: Laser ablation of a flat aluminum metal target (without using the bath gas/supersonic expansion technique) was used to generate aluminum cluster anions containing from 3 to 50 atoms. The structures and reactivities of Al$_n^-$ for n = 3–23 were then probed with the use of Fourier transform mass spectrometry. Charge exchange reactions were used to bracket the electron affinities of these clusters, which were in good agreement with other theoretical and experimental values. Collisional dissociation of Al$_n^-$ for n = 3–13 indicated elimination of neutral aluminum atoms for all cluster ions, except Al$_7^-$, Al$_6^-$, and Al$_3^-$, which fragmented primarily by electron detachment. Aluminum cluster ions are unreactive with CH$_4$ and N$_2$O, but the small cluster ions will react with O$_2$ to generate AlO$_2^-$ and AlO$^-$. For clusters containing more than eight aluminum atoms, the even-numbered clusters react much more rapidly than the odd-numbered clusters with oxygen to form AlO$_2^-$ and AlO$^-$.

The investigation of neutral and ionic metal clusters is of considerable interest since these compounds may serve as models

for studying the nature of catalysis and related processes.[1] The generation and reactions of positively charged clusters, such as