

# Benzene, Aromatic Rings, Van der Waals Molecules, and Crystals of Aromatic Molecules in Molecular Mechanics (MM3)

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*Received 19 February 1987; accepted 31 March 1987*

Benzene has been studied with the MM3 force field, first as a monomer, then as a van der Waals dimer, then in the crystal. The non-bonded aromatic portion of the MM3 force field has been derived to fit reasonably well the known properties for the above. The force field includes dipoles of 0.6 and 0.9 D for  $C_{sp^2}-H$  and  $C_{sp^2}-C_{sp^3}$  bonds, respectively. The benzene dimer is calculated to have a lower energy when perpendicular, than when eclipsed face to face. The crystal of benzene has a herringbone pattern with correct cell constants and heat of sublimation, while hexamethylbenzene as the dimer and in the crystal has a skewed-stack of pancakes type structure, as observed.

Molecular mechanics has become a widely used technique for studying various chemical problems.<sup>1</sup> The MM2 force field<sup>2</sup>, developed in 1976–1977, has been widely used, and has been found to be applicable to large numbers of compounds and chemical problems. However, studies on a number of strained or unusual compounds have shown that MM2 is not always adequate for dealing with such substances. A molecular mechanics force field is formally derived from a Taylor's series expansion of the potential energy surface, and is normally formulated as a power series involving internal molecular coordinates.<sup>1</sup> Just which terms are important in the force field, and the values for the parameters to be used in the force field, are established by fitting to available data.<sup>3</sup> If the available data span too limited a set of molecules, then that set of molecules can be well fit, but extrapolations lead to less satisfactory results. In the ten years since MM2 was developed, many data concerning strained and unusual molecules have become available, and various alternatives for dealing with these new data have been considered. It would be possible to upgrade MM2 by changing some of the internal parameters. The disadvantage of this approach is that the MM2 results obtained with the new program would then not be comparable with those obtained previously. While some incompatibility of this kind might be acceptable if the improvement were suf-

ficient, we have considered that it might, at this point, be preferable to go back and redevelop a completely new force field (MM3). Actually, since MM2 works well for many things, the new force field would not be expected to differ dramatically from MM2, but it would be best if MM3 not only contained re-optimized parameters, but also contained new functions as well. We are still satisfied that the original parameters in MM2 are about as good as one can do with the equations and other limitations originally imposed. Osawa has published<sup>4</sup> what he calls an "improved force field" for MM2, but in our opinion, he has simply moved the error from one place to another, and the error still remains. Whether this constitutes an improvement is a matter of preference, and depends on whether the user is working primarily with problems from which the error has been moved away, or with problems where the error has now been increased.

We have identified several different significant changes that have to be made in MM2 to fit the now available data. Osawa also independently identified some of these.<sup>4</sup> Of course, when some things are changed in a force field, then other things must be changed, because the parameters are all correlated. It turns out that MM3 is a little bit different from MM2 in most respects, and quite a lot different in a few points. The development of MM3 parallels that of MM2 in many respects. The data

base used was much larger for MM3, and vibrational information has been used as well. The results are sufficiently extensive that they will be reported in a series of publications. The first of these was devoted to the torsion-stretch interaction.<sup>5</sup> This article will be concerned only with nonbonded interactions in MM3.

Nonbonded interactions are usually broken down into electrostatic and van der Waals. Important quantities to establish in any force field are the van der Waals parameters. This was done in MM2 for hydrocarbons by considering the crystal structures of graphite, diamond, and *n*-hexane, in addition to many molecular structures. In formulating MM3, we carried out the evaluation of the van der Waals parameters more carefully than previously, and we have studied in more detail the crystal packing in several different hydrocarbon molecules. We examined a series of normal alkanes with the intention of optimizing the unit cell parameters and the heats of sublimation by adjusting the van der Waals parameters for carbon and hydrogen. Because these compounds have low melting points, and are flexible, they offer some complications for present purposes in relating the calculations to the experimental data. However, we were able to fit the structures of these crystals, and their heats of sublimation, considerably more accurately than we did with MM2.<sup>6</sup>

At the same time that we studied these alkane crystals, we also studied aromatic crystals, specifically benzene, hexamethylbenzene, and a few others. Graphite<sup>7</sup> and diamond<sup>8</sup> were also examined, as previously mentioned. We were also guided in this work by the structures of some compounds that have recently become available in which two hydrogen atoms are pushed very close to one another.<sup>9</sup> While that portion of the work will not be described herein, it puts constraints on just how large the force interacting between hydrogens can be at very short distances. It has been established that for distances less than about 2 Å, this force becomes too great in MM2.<sup>4,9,10</sup> From these studies, we feel that we now have a better set of van der Waals parameters for carbon and hydrogen than we had in MM2.

The present article will describe the studies on the aromatic compounds mentioned. In the course of these studies, it was found that it

was necessary to put electrical charges into the carbon-hydrogen bonds in benzene and in alkenes. We are now satisfied that the advantages of introducing electrostatic terms in such molecules outweigh the disadvantages of more computation time, and more parameters that are required. As with MM2, we will express our electrostatic interactions in terms of dipole-dipole interactions (also charge-charge, and charge-dipole in cases where net charges are present). It may be wondered if charge-charge interactions can be used to represent the electrostatic situation in an ordinary molecule with more or less accuracy than dipole-dipole interactions can be used. We studied this problem somewhat superficially in the 1960s, and could find no compelling reason to choose either of these representations over the other.<sup>10</sup> Charge-charge interactions are more quickly computed because the geometric constructions needed for dipole-dipole interactions are avoided. On the other hand, the number of charges is greater. Perhaps more important, the dipole-dipole interactions fall off as  $1/r^3$ , whereas charge-charge interactions fall off only as  $1/r$ . In large molecules, therefore, one must carry the latter interactions to much longer distances before cutting them off.<sup>11</sup> We have decided to keep the dipole-dipole formulation in MM3, not because we are convinced that it is any better, but mainly because it is easier to carry over the previous results. We have assigned non-zero values to the bond moments for both  $C_{sp^2}-H$  (0.6 D) and  $C_{sp^2}-C_{sp^3}$  (0.9 D). The  $sp^2$  carbon is the negative end of the dipole in each case. With such dipoles, one can more realistically explain things like hydrogen bonding to an alkene, and in particular, one can obtain the results to be described in this paper. In MM2 the  $C_{sp^2}-H$  bond was taken to be electrically neutral, since in the earlier studies we had not yet found any data which required the addition of charges. But more recently, having examined the data on the benzene crystal and on the benzene dimer, we have accepted the point made much earlier by Williams<sup>12</sup> that one cannot fit the benzene crystal data without using charges, and we have introduced these into MM3 (as dipoles). We still retain the carbon hydrogen bond of alkanes as nonpolar. We have examined quite a lot of structural data for alkane compounds, with and without charges being included, and

we have not found any case in which we could fit the structure better using charges than we can fit it without charges. Certainly, *ab initio* calculations show that there are charges in such bonds.<sup>13</sup> However, the definition of charge in that case is sufficiently far removed from the charge model that we use that it is not certain if the use of charges in molecular mechanics for aliphatic hydrocarbons is either necessary or desirable. Our view has always been, and continues to be, that we keep the force field as simple as possible, adding extra terms only when they are clearly required by the data we're trying to fit.

After this work was completed, we learned from Drs. Pettersson and Liljefors that they had reached similar conclusions regarding charges in aromatic compounds from considering data on the benzene dimer, and that they had modified MM2 to account for these data.<sup>14</sup> They used point charges, whereas we used point dipoles to accomplish the same end. Using the known C—H bond length, if we convert their point charges to point dipoles, their values are nearly identical to ours.

We considered the benzene dimer problem in some detail. With MM2, the benzene molecules have a lower energy if they have a regular face-to-face or stack-of-pancakes arrangement, as opposed to any other arrangement, including the T shape. The reason for this is evident; the van der Waals attractions are much greater, because more atoms are in contact. Without electrostatics, using only van der Waals forces, there appears to be no possible formulation of the forces such that the T shaped dimer would be more stable. Electrostatics manages this by putting the positive hydrogen into the center of the negatively charged carbons. Thus, the T shaped dimer is greatly stabilized by electrostatics. Simultaneously, the stack-of-pancakes dimer is destabilized, because here the positive and negative charges are exactly above one another. (In the dipole formulation, the dipoles are aligned parallel and pointed in the same direction with the same results.) The skewed stack-of-pancakes dimer is more stable than the ordinary stack, however, as long as the dipoles exceed a threshold value. This may be contrasted with the case of hexamethylbenzene. For this compound in our formulation, the dipoles are only in the C<sub>sp<sup>2</sup></sub>—C<sub>sp<sup>3</sup></sub> bonds;

the methyl carbon bears a positive charge, and the benzene ring carbons a negative charge.<sup>14</sup> But the T-shaped dimer for this molecule is not so favorable, because the methyl hydrogens hold the positive end of the T quite far out away from the center ring carbons of the other molecule. So in this case, the skewed-stack dimer becomes much more stable.

The van der Waals potential for two atoms interacting with each other, and not bound together nor to a common atom, is given by the following expression in MM3:

$$E_{\text{vdw}} = \sqrt{\epsilon_1 \epsilon_2} (1.84(10)^5 e^{-(12.00/P)} - 2.25P^6) \quad (1)$$

where  $\epsilon$  is the energy parameter relating to the depth of the potential well for the atom, and  $P$  is the distance between atomic centers (or between offset centers for hydrogen) in units of the sum of the van der Waals radii of the atoms. The total nonbonded interaction energy is ( $E_{\text{vdw}} + E_e$ ), where  $E_e$  is the electrostatic energy.

In order to study benzene, and aromatic molecules, as they combine into dimers and crystals, one must first know what the monomer looks like. The benzene monomer in MM3 has a bond length (1.399 Å) which was chosen to fit the  $r_g$  value known experimentally.<sup>15,16</sup> The C—H bond length calculated is 1.104 Å, again chosen to fit experimental data.<sup>15</sup> As in MM2, we represent the anisotropy of the hydrogen by offsetting its center for purposes of the van der Waals interaction, moving it inward along the C—H bond so that instead of being 1.000 of this bond distance out from carbon, it is only 0.923 of this distance out. With this correction used to take care of the anisotropy, the atoms are treated as spherical. The van der Waals parameters for hydrogen were arrived at largely by a study of alkanes and alkenes, and we will simply give the results here. The van der Waals properties for carbon were arrived at by treating graphite by the methods previously described<sup>7</sup>, and they differ little from those obtained for MM2. The numerical values for the van der Waals parameters obtained for use in eq. (1), are as follows: C: (type 2, sp<sup>2</sup> hybridized)  $r_{\text{vdw}}$  1.96 Å,  $\epsilon$  0.056; H: (type 5)  $r_{\text{vdw}}$  1.62 Å,  $\epsilon$  0.020.

Force constants for bending and stretching were established from structural studies, plus a consideration of the vibrational spectra of

some simple molecules. In the present work, we are simply taking the benzene molecules to be rigid, and we are considering how benzene molecules orient themselves to form dimers or crystals, and hence the internal molecular force constants are not of concern here, and they will be discussed elsewhere.

Having then established the nature of the benzene molecule for use in MM3, and having previously established the MM2 representation of the molecule, we carried out studies, first of the benzene dimer. It is known that a benzene dimer detected in molecular beam experiments has a dipole moment, and therefore it must have a structure sufficiently lacking in symmetry to yield that result.<sup>17</sup> It is also known from spectroscopic studies that there exists a second dimer in which the benzene rings are slipped and parallel.<sup>18</sup> The relative stabilities of these two dimers is somewhat uncertain. *Ab initio* calculations,<sup>19</sup> with some configuration interaction to account for the electron correlation, have indicated that the perpendicular dimer is more stable than the parallel one. A study on the second virial coefficients of benzene gas has given qualitatively similar,<sup>20</sup> but quantitatively quite different results. MM2 calculations indicate that the parallel dimer is much more stable than the perpendicular one, and that the latter does not correspond to an energy minimum.

A consideration of the two dimers and of properties of van der Waals interactions indicated to us that the parallel dimer would necessarily be calculated to be more stable than the perpendicular one, independent of the exact numerical values chosen for the van der Waals parameters, if the only interaction considered was of the van der Waals type. This is simply because more atoms can come closer together in the parallel arrangement. Hence, it is impossible with the MM2 formulation to get the qualitatively correct result.

Williams showed many years ago in studies on the benzene crystal, that it is necessary to include electrostatic interactions between the molecules in order to get a proper crystal geometry. It seemed reasonable that the same was true here. Assigning charges (hydrogen positive, carbon negative) or the equivalent (which is what we have done in our formulation) of placing point dipoles in the C—H bonds (with hydrogen at the positive end) and giving them a value of 0.6 D, clearly has a

qualitatively correct effect on the benzene dimer problem. The two benzene molecules in the face-to-face dimer have like charges as neighbors, so that the energy of this situation is increased. The perpendicular dimer, on the other hand, places a positive charge down into the middle of the negatively charged carbons, and this situation is stabilized. We considered making appropriate changes in MM2 in order to appropriately represent these facts. However, we decided against it for certain reasons. First, MM2 has been very widely used, and a sweeping change of this kind at this point would make all future calculations with the revised program incompatible with those of the earlier program. Since few people are interested in such things as benzene dimers or crystals, we thought that an *ad hoc* correction could be made if anyone is interested, however we decided not to change the MM2 program itself.<sup>21</sup>

On the other hand, since we are now just developing MM3, we decided to take this opportunity to put this charge distribution into the force field at the outset. We will describe below three different sets of molecular mechanics calculations; MM2 calculations, MM3 calculations without charges, and MM3 calculations, with charges, as they will be in the program when it is made publicly available.

Figure 1 shows the energies of the benzene dimer face-to-face, as determined experimentally, and by the various kinds of calculations. Curves *a* and *c* give the *ab initio* calculations and experimental results, and so something in this vicinity is what we wish to reproduce. MM2 gives curve *e*, which is reasonable in terms of geometry, but the attraction is seen to be much too great. In MM3 without the charges, we obtained curve *d*. This is a step in the right direction, but the attraction is still much too great. However, when the dipoles are added we obtain curve *b*, which now falls in between the two curves we are trying to match.

Next, turning to the perpendicular dimer, curves *a* and *c* in Figure 2 are what we are trying to match, whereas MM2 gives us curve *e*. Here, the geometry is poor, the centers of mass of the molecules are about 1 Å too far apart. Also, the attraction is not nearly strong enough. If we go over to the MM3 formulation without charges, we get curve *d*, which is improved both in geometry and in energy, but is

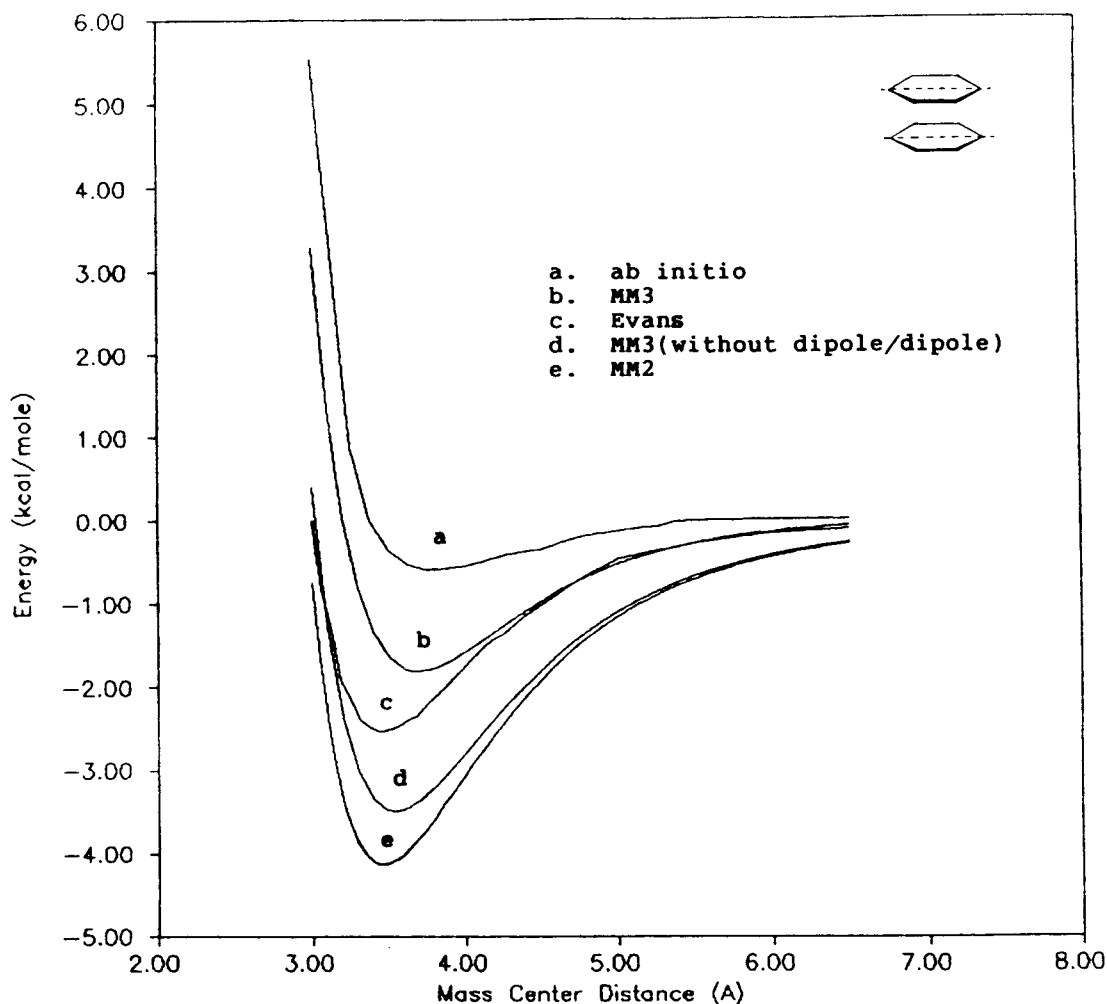


Figure 1. The benzene dimerization potential curves for MM2, MM3 and other calculations.

still not very good. However, adding the charges we get to curve *b*. The distance between centers in the dimer is still somewhat too great, and the attractive energy is not great enough, but the results are clearly much better than they were for MM2.

Can we do this calculation better? We could, if we were sure just what it was we wanted to do. Part of the problem is that there is a wide discrepancy between the *ab initio* results and the experimental results. Second, it is not at all clear what the geometries of the dimers in question really are. We have other reasons for choosing the values for the dipoles which we have introduced in MM3, and so, we will simply say here that MM3 reproduces the information on the benzene dimer much better than MM2 does, even though it may not be as good as one would like. But there are other problems. We have adopted the policy of using an effective dielectric of 1.5 for all electrostatic calculations in MM2 for molecules in the gas phase, and we have carried over that

value here. It is an arbitrary approximation, taking into account the fact that in molecules in general, the charges are not separated by a vacuum, but by other parts of the molecule, and hence, one needs an effective dielectric constant of something greater than unity. In the present work, reducing this value from 1.5 towards unity would improve the fit for the results that we are trying to obtain. However, our goal is really to develop the MM3 force field to be as useful as possible, particularly for the calculation of energies and geometries of molecules. Hence, we feel that the outcome of the dimer calculations are adequate for present purposes, although clearly they could be improved if one were specifically interested in the benzene dimer.

There is one other item to be mentioned. In the *ab initio* calculations on the benzene dimer, only partial geometry optimization was reported. In our calculations we optimized the geometries, but with respect to certain constraints of symmetry. When we

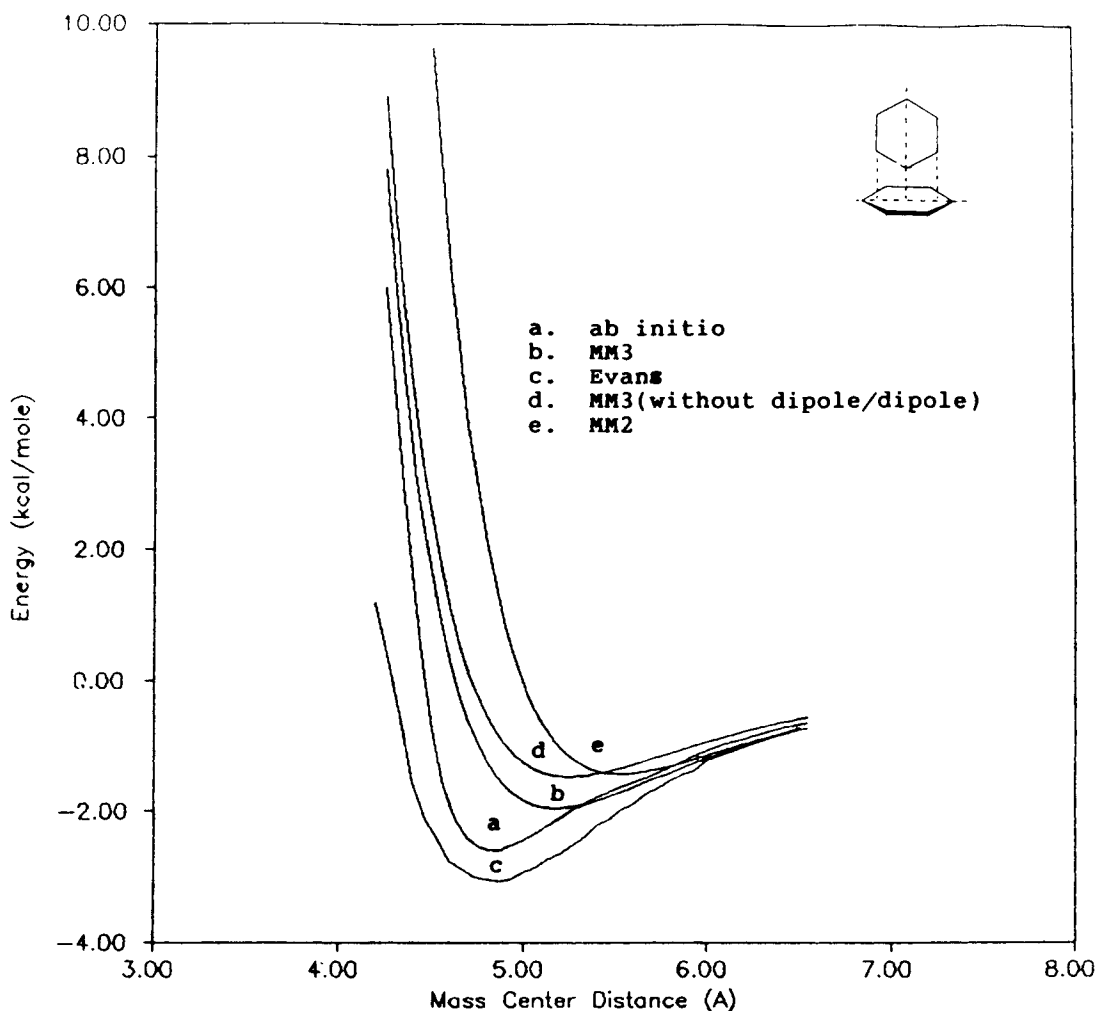


Figure 2. The benzene dimerization potential curves for MM2, MM3 and other calculations.

looked at the eigenvalues of the force constant matrix, we found that with MM2, while the parallel dimer does represent an energy minimum, the perpendicular one does not. And if the symmetry constraints are removed, the perpendicular one will go over to the parallel one. With MM3, neither of these arrangements corresponds to an energy minimum. There is an energy minimum where the benzene rings are parallel, but skewed. This still manages to put positive charges near negative charges, but gives larger van der Waals attractions as well. On the other hand, the perpendicular dimer has two negative eigenvalues in the force constant matrix. If one ring is tilted with respect to the other, then there is only one negative eigenvalue. Thus, the structure represented by the perpendicular dimer is really a hilltop, and the flipping over of one ring from the parallel skewed conformation to its mirror image can go by one ring going up over the top of the hill, or the ring can go around the hill in a skewed path

in either direction, through a valley. To match with what we believe to be experimentally observed, there should be a dip in that valley, so that the perpendicular, but now off center, dimer lies at an energy minimum instead of a maximum, but the difference here is only a small fraction of a kcal, and is charge and dielectric constant dependent. Hence, we feel again that our description of this situation is adequate for our purposes.

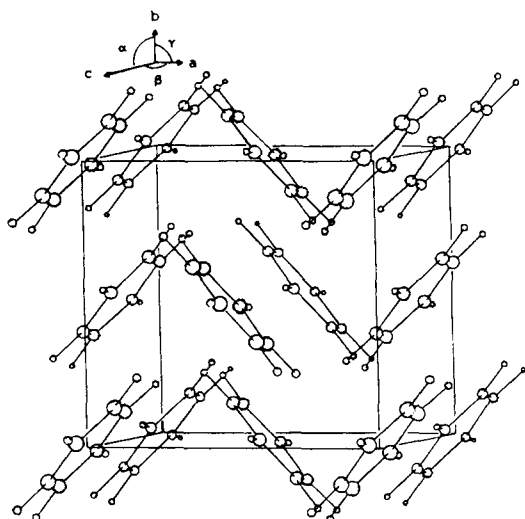
Next, we looked at the benzene crystal. Our crystal is represented by 108 molecules (27 unit cells), made up initially by packing either the parallel or the perpendicular dimers together. Indeed, we found with MM2 that there are two separate minima (polymorphic crystals), which correspond to different crystal lattices. Unfortunately, MM2 finds that the parallel dimer gives a much more stable crystal. The perpendicular dimer gives a crystal that has a pretty good geometry and energy, but since the parallel structure gives a much more stable crystal, this is

**Table I.** Unit-cell parameters and heat of sublimation for benzene.

Parameters	MM2	MM3	Exptl. [a]	Dev. (%) [b]
a	6.75	7.07	$7.03 \pm 0.02$	0.6
b	7.14	7.18	$7.46 \pm 0.02$	-3.8
c	9.52	9.82	$9.67 \pm 0.02$	1.6
alph	89.6	85.5	$90.0 \pm 0.3$	-5.0
beta	90.8	90.7	$90.0 \pm 0.3$	0.8
gamma	89.3	90.1	$90.0 \pm 0.3$	0.1
vol	459.0	493.2	$507.1 \pm$	-2.7
Esub	11.18	10.32	10.42	-0.1

<sup>a</sup> E. G. Cox, F. R. S., D. W. J. Cruickshank and J. A. S. Smith, *Proc. Roy. Soc. (London)*, **A247**, 1 (1958).

<sup>b</sup> (MM3-Exptl.).

**Figure 3.** The benzene crystal packing calculated with MM3.

not in agreement with experiment. For calculation of the heat of sublimation, a crystal composed of 15 unit cells on a side was used. The lattice vibrations were neglected.

The perpendicular dimer with MM3 gives a very good crystal, with a heat of sublimation and unit cell parameters that agree quite well with experiment. The parallel dimer, on the other hand, is a crystal with a lower heat of sublimation, and hence is less stable, but only by 0.3 kcal/mol.

The crystal packing diagram calculated with MM3 is shown in Fig. 3. The pertinent crystal parameters calculated with MM2 and MM3 are summarized in Table I.

These calculations have been extended to many other aromatic molecules, and crystals derived therefrom. This work will be reported separately later.

The authors are grateful to the National Science Foundation and to the National Institutes of Health for support of this work. (Grant numbers, NSF-CHE8315543 and NIH-R24RR02165, respectively.)

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