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Prediction of crystal structures *

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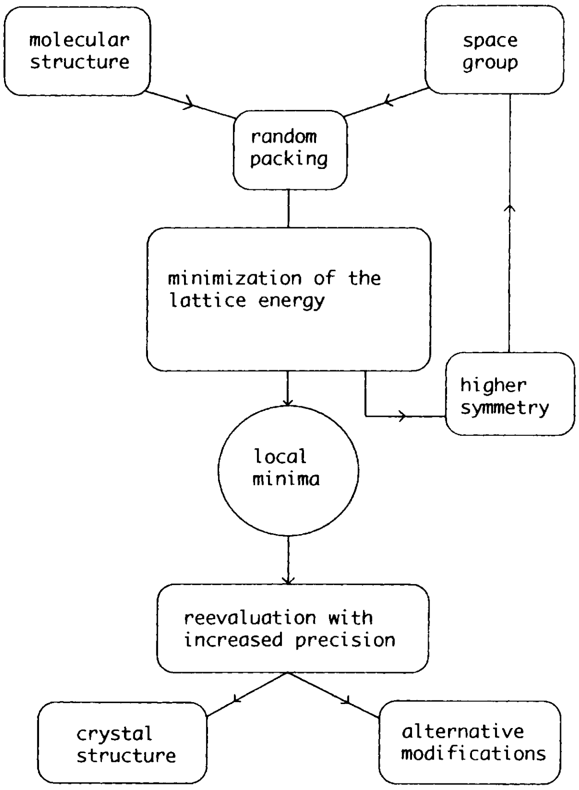
The atom–atom potential method has been demonstrated to quantify intermolecular interactions in molecular crystals of organometallic compounds. A sufficiently general minimization program with a robust steepest-descent algorithm has been used successfully to show that experimentally determined crystal structures correspond to energy minima. The algorithm may be used to predict hitherto unknown crystal structures starting from random packings.

Many physical properties of materials are governed by their solid-state structure. In the field of molecular crystals, single-crystal X-ray diffraction has made enormous progress towards automatization and as a result the step from synthesis to structure has almost become routine. Structure prediction is a topic of current research. Possible applications like ferroics, pigments, or non-linear optics are not the only aims of this development: from the viewpoint of basic research, molecular crystals are supramolecules and very apt to the study of molecular recognition; crystallization provides countless examples of self-assembly. Close packing and, as a consequence thereof, the preference for only a few very common space groups[1] was recognized many years ago by Kitaigorodsky[2] as general principles in molecular crystals. Especially in the realm of organic crystal chemistry, the atom–atom potential method[3] provides a quantitative approach to the lattice energy of molecular crystals. The program OPEC (Organic Packing Energy Calculations),[4] has become a widely used tool in organic solid-state chemistry. Lattice-energy minimizations requiring a reasonable starting geometry are implemented in several well known computer programs, *e.g.* Busing's WMIN[5] and Williams' PCK 83.[6] Among possible applications of lattice-energy minimizations the prediction of crystal structures has for long been one of the most ambitious aims of this method.[7] Owing to obvious limitations in computing facilities, only problems with a few degrees of freedom could be handled in the past.[8,9] In the last years, the problem of complete structure predictions from scratch has been tackled again by the recent approaches of Gavezzotti ('cluster method')[10] and Karfunkel and Gdanitz.[11] Braga and Grepioni[12,13] successfully transferred the methods of organic crystal chemistry like lattice-energy calculations to organometallic compounds. Making use of the cluster method, they were able to reproduce the crystal structure of [Fe(CO)$_5$] cor-rectly.[14] In this contribution, we present a method for the prediction of crystal structures of organometallic compounds which is based on lattice-energy minimization starting from random packings. In well ordered crystals, entropy differences between different packing arrangements are small; thus minima in lattice energy will correspond to minima in free energy. The latter represents the decisive stability criterion for a crystal structure.

Method

General

The crystal structure is obtained from an input molecular structure by minimizing the intermolecular energy. Starting from random molecular arrangements which include crystal symmetry, minimization is achieved by a steepest descent algorithm. Scheme 1 represents a flow chart of the method.



Scheme 1

Molecular geometry

As the precision of the molecular structure is not crucial, the input may be obtained by a variety of computational or experimental methods (X-ray crystallographic determination, electron diffraction, microwave spectra, *etc.*). Standard molecular modelling procedures may be helpful to combine these types of information. When X-ray data are used, the structures may be idealized, *e.g.* by averaging over chemically equivalent and crystallographically independent distances and placing hydrogen atoms in calculated positions. For molecules with internal degrees of freedom different conformations have been treated separately; in principle, our approach may be combined with an intramolecular force field to locate the overall free-energy minimum of the crystal packing and molecular conformation.

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* Application of the Atom–Atom Potential Method to Lattice-energy Calculations for Organometallic Compounds. Part 1.

Packing variables

Along with molecular structure data, the input for the minimization procedure requires two different types of information on the intermolecular arrangement. Space group symmetry (see below) is maintained over the whole minimization procedure. In addition to this static information, the unit-cell dimensions, the position and the orientation of each symmetry-independent rigid molecule are variables which determine the lattice energy. These latter parameters are assigned random values within a user-defined range at the start of the minimization procedure and are subsequently refined (see below).

Symmetry

The crystal symmetry is included from the beginning. For applications like structure prediction where in general no *a priori* space-group information is available, possible space groups have to be tested separately. Fortunately, only a very limited number of space groups occur in practice: more than 87% of all molecular crystals belong to one of the most common 12 space groups.[15] The strong preference for 'antimorphism'[16] with only a few independent molecules and the possibility to reach higher symmetry during the minimization procedure reduces the number of space groups that have to be considered for practical applications. In contrast to other methods, our minimization procedure allows calculations in all space groups with molecules occupying every kind of special position, including 'complicated' cases like space group $Pa\bar{3}$ with molecules on the three-fold axes.

Van der Waals energy

Van der Waals (vdW) forces are the predominant contribution to the lattice energy of molecular crystals. They may be calculated by the atom–atom potential method, which has proven a successful tool in organic crystal chemistry: intermolecular vdW forces are reduced to a summation over discrete pair interactions in which the interaction energy depends only on the atom types of the centres involved and the distance between them. In our implementation of this method, we use a Buckingham potential of the type (1) where r_{ij}

$$E_{\mathrm{vdw}} = \tfrac{1}{2}\sum_{i}\sum_{j} - Ar_{ij}^{-6} + Be^{-Cr_{ij}} \qquad (1)$$

represents the interatomic distance and A, B and C are empirical parameters. The summation in principle extends to infinity and must in practice be limited to a user-defined cut-off radius (*e.g.* 20 Å). Different sets of empirical interaction parameters have been published,[17–19] and both their numerical values and the lattice energies obtained by their application differ considerably, whereas the minimizations converge to quite similar crystal structures. This behaviour is obviously due to high correlation between the parameters. Therefore care must be taken when combining different parameter sets from the literature. Table 1 summarizes the parameters used in our minimizations.

Electrostatic energy

Even though van der Waals forces constitute the major contribution to the lattice energy, Coulomb interactions may be decisive for the preference of one molecular arrangement over others of similar energy. Their influence may be included in our calculations using the normal Coulomb formula (2). The

$$E_{\mathrm{ei}} = \tfrac{1}{2}\sum_{i}\sum_{j}\frac{1}{4\pi\varepsilon_{\mathrm{r}}\varepsilon_0}\cdot\frac{q_i \cdot q_j}{r_{ij}} \qquad (2)$$

relative permittivity ε_{r} is set to the value for a vacuum, 1.0, and point charges q_i and q_j are assigned to the atomic centres. This strategy is rapid and simple because both the atomic positions and the interatomic distances are also required for the calculation of vdW interactions. The summation includes five unit cells in each direction. Unlike in ionic solids, the charges involved in our minimizations are small (see below) and do not generally require convergence acceleration by a summation in reciprocal space as in the methods of Ewald,[20] Bertaut[21] or Williams.[22] Unsatisfactory convergence behaviour of the summation in real space is only a serious drawback when polar molecules in polar space groups have to be tested, because they may exhibit a non-zero unit-cell dipole moment. In these cases the summation may be extended to any user-defined range over whole unit cells at the expense of longer calculation times.

To obtain point charges for our organometallic compounds we make use of the extended Hückel method[23] with charge iteration. The resulting charges may be scaled with an additional factor to match our vdW potentials. An empirical scale factor of 1.1 proved appropriate in the case of our compounds.

Minimization

We use a simple and robust steepest-descent procedure for the lattice-energy minimizations starting from random packing of the molecules. Depending on the crystal system and the space-group symmetry, up to six lattice constants ($a,b,c,\alpha,\beta,\gamma$) and a maximum of three translational and orientational parameters for each independent molecule have to be specified to define the packing. Upper and lower limits for the random start points of the lattice constants a, b and c should ensure a very loose arrangement of the molecules, *e.g.* approximately twice or three times the expected final values, to allow for reorientation of the molecules during the energy minimization. The translational and orientational parameters are restricted to the independent part of the lattice-energy hypersurface, *e.g.* only obtuse monoclinic cells are considered. As an advantage of our method, additional *a priori* information may be used from the beginning: lattice constants from a successfully indexed powder diagram or knowledge about packing motifs or the preferred

Table 1 Parameters for the van der Waals potential

Interaction	A/kJ mol^{-1} Å^{-6}	B/kJ mol^{-1}	C/Å^{-1}	r_0/Å	r_{min}/Å	E_{min}/kJ mol^{-1}	$\lambda = Cr_{\mathrm{min}}$
H···H	144.2	11 104	3.74	2.831	3.229	−0.064	12.08
C···H	523	36 677	3.67	2.897	3.303	−0.203	12.12
C···C	2 377	349 908	3.60	3.451	3.882	−0.396	13.98
O···O	1 242.6	372 203	4.18	2.885	3.253	−0.586	13.60
Si···Si	9 702	1 542 969	3.46	3.763	4.218	−1.015	14.59
Fe···Fe	6 463	1 804 000	4.00	3.110	3.498	−2.016	14.00

r_0 = Distance where $E = 0$; r_{min} = minimum of the potential curve; E_{min} = depth; λ = steepness; all other mixed parameters were calculated according to the combining rules.

orientation of the molecules may reduce calculation times drastically. After the minimization algorithm has located a local energy minimum, new random values are generated for all packing variables. From a total of 500–1000 minima, those packings with the most favourable lattice energy are re-evaluated with increased accuracy. As a rule, the best minima are found several times from different starting points. After generation of the appropriate input, the minimization procedure is run automatically.

Computational details

For the vdW potentials, the combining rules $A_{12} = (A_{11}A_{22})^{\frac{1}{2}}$, $B_{12} = (B_{11}B_{22})^{\frac{1}{2}}$ and $C_{12} = (C_{11} + C_{22})/2$ have been respected throughout our calculations. Our interaction parameters are essentially based on the results of Williams.[6,17,24] Parameters for oxygen were taken from Mirsky[18,25] and modified in the following way to match our potentials: crystal structures with essentially C $\cdots$ C, C $\cdots$ H and H $\cdots$ H intermolecular contacts showed no significant differences in their lattice constants after minimization with Mirsky's parameters and our own parameter set; their lattice energy, however, resulted in more favourable values (minimum 12%, maximum 17%, average 14.5%) for our parameters. This means that Mirsky's parameters A and B which are responsible for the depth of the interaction curve must be adjusted accordingly to avoid underestimation of the interactions involving oxygen atoms, whereas C, characteristic of the radial position of the minimum of the potential-energy curve, may be retained. Scaling of Mirsky's A and B with a factor of 1.145 resulted in the potential parameters listed in Table 1. Metal parameters are not a crucial point and are largely intuitive. To allow for at least a reasonable extrapolation of parameters for larger atoms, those for silicon were derived and tested: C(Si $\cdots$ Si) was set to an extrapolated value of 3.46 Å, and A(Si $\cdots$ Si) and B(Si $\cdots$ Si) were obtained from a least-squares fit to the crystal structure of hexasilylbenzene.[26] The parameters obtained were tested reproducing the crystal structure of 2,2,6,6-tetrasilyl-1,3,5,7-tetrasilaspiro[3.3]heptane.[27] Parameters for metals were obtained by extrapolation.

Within a cut-off distance of 10 Å, at least 90% of the vdW energy is included. For more accurate calculations, interactions of up to 20 Å are taken into account, corresponding to more than 99% of the vdW energy calculated for an infinite cut-off. Further extension of the threshold does not change the order of precedence between different minima of similar energy.

Owing to the mathematical form of the Buckingham potential, the attractive r^{-6} term overrides the repulsive exponential contribution for very small interatomic distances (*e.g.* C $\cdots$ C < 0.6 Å). To avoid this artefact and ensure a realistic repulsive interaction, we replace the calculated potential energy by a constant value of $+10^6$ kJ mol^{-1} for interatomic distances of less than 1.3 Å.

For the input molecular geometries we used electron diffraction data in the case of $[Fe(C_4H_4)(CO)_3]$ **5**.[28] The metallocene $[Fe(C_5H_5)(C_5Me_5)]$ **6** was constructed by combining the ring geometries and the iron–ring distances from $[Fe(C_5H_5)_2]$ and $[Fe(C_5Me_5)_2]$. For the other compounds, X-ray diffraction data were used; they are individually referenced in the corresponding tables.

Extended Hückel calculations were performed with the program ICON[29] making use of the charge-iteration procedure. Parameters for C, H, N, O, Si, and the first-row transition metals were taken from ref. 29, orbital parameters for Nb and Rh from Summerville and Hoffmann,[30] for Ru from Basch and Gray[31] and charge-iteration parameters for Nb, Rh and Ru from Munita and Letelier.[32] With a convergence limit of 0.000 01 Å for lattice constants and a cut-off distance of 20 Å, the reproducibility for the same minimum reached from different random starting points was better than 0.001 Å. As this value exceeds by far the precision of our method (*cf.* Results and Discussion), reproducibility is not a limiting factor in our calculations.

The minimization programs are written in ANSI-C and run under common operating systems like DOS, VAX-VMS, or UNIX. Calculation times are of the same order of magnitude as for other methods of crystal structure calculation: the structure prediction for the metallocene **6** required about 2d of computer processing time on a fast single-processor computer (*e.g.* DEC9000). In addition, our method still needs considerable user interaction as far as the preparation of the input molecular structure and charges and the interpretation of the possible packings are concerned; with increasing computer speed, these will probably be the true limitations in the future.

The coordinates of all input molecular geometries and calculated crystal structures may be obtained from the authors upon request.

Results and Discussion

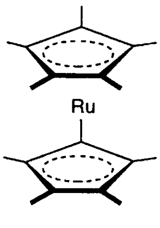
In all test cases where our method was applied to organometallic compounds and the correct space group information was supplied the experimental crystal structures were correctly reproduced starting from random packings. Calculations were performed on a total of 25 organic and organometallic compounds.[33] Table 2 gives four examples and allows the comparison between calculated and experimental structural data. A common feature of our calculations is a slight underestimation of the lattice constants. The observed discrepancies typically amount to *ca.* 0.3 Å in lattice constants and about 1° in angles.

Our results confirm that the space-group problem may be overcome: statistics show that the great majority of molecular crystals adopt space groups which are 'antimorphic' or 'tending towards antimorphism' in Wilson's nomenclature;[16] therefore only a few probable space groups have to be considered for most purposes. During the minimization procedures additional symmetry can emerge: this may occur either by a reduction of the number of independent molecules or by a transition into a supergroup of the current space group with the molecules in special positions. The second case may be illustrated by the subgroup–supergroup relations between $P2_1/c$ *versus* $C2/c$ or *Pnma*. The latter space groups are the most common ones for molecules with site symmetry 2 or *m*. This relation implies that the higher symmetry should not necessarily be included in the space group-testing strategy but can be found 'automatically'. Minimization of the $[Ni(CO)_4]$ molecule in a subgroup provides a good example: the experimentally established space group[38] is $Pa\bar{3}$ with molecules on Wyckoff positions 8*c*, *i.e.* site symmetry 3, and $a = b = c = 10.832(5)$ Å. Minimization in the subgroup *Pbca* (a quite common space group) converges at $a = 10.256$, $b = 10.254$, and $c = 10.253$ Å with the Ni less than 0.001 Å off the idealized position in the cubic space group. An additional example illustrating the numerical relations between minimum structures in both the correct space group and a subgroup is given in Table 3 where the results for the butadiene complex **5** are compiled.

In principle, all crystal structures could be treated as having space group $P1$ with a sufficiently high number of independent molecules, but this approach would require lengthy calculations and elaborated search algorithms for 'missed' symmetry.

The crystal structure of the metallocene **6** is successfully reproduced from an approximate molecular geometry input and without any *a priori* lattice-constant or space-group information. Both staggered and eclipsed conformations corresponding to the extrema of a 'soft' conformational degree of freedom were investigated separately in the common space groups $P1$, $P\bar{1}$, $P2_1/c$ with a molecule in general position and in $P2_1/m$ and *Pnma* with a molecule on the crystallographic

Table 2 Comparison between experimental and calculated lattice constants in four organometallic compounds on the basis of van der Waals and, in the case of **4**, electrostatic interactions



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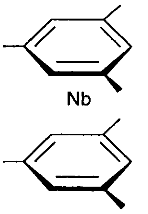

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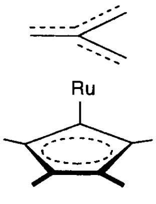

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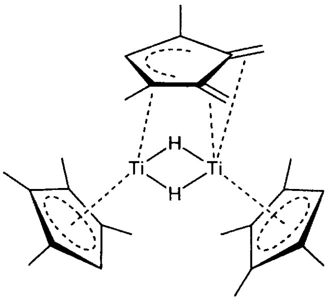
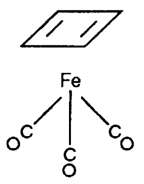


4

	Ref.			
Parameter	34	35	36	37[a]
Space group	$P2_1/m$	$P\bar{1}$	$P2_1/c$	*Pnma*
Lattice constants[b]				
a/Å	7.718 (7.617)	9.796 (9.509)	8.516 (8.306)	8.292 (8.230)
b/Å	14.646 (14.303)	10.822 (10.787)	22.078 (22.014)	15.351 (14.948)
c/Å	8.617 (8.527)	8.724 (8.520)	8.559 (8.062)	18.268 (18.229)
α/°		107.64 (107.66)		
β/°	106.50 (107.80)	113.77 (113.78)	119.83 (119.06)	
γ/°		91.49 (92.05)		
Metal coordinates[b]				
x	0.080 (0.083)	0.2828 (0.2765)	0.2473 (0.2151)	0.5966 (0.5943)
y	0.250 (0.250)	0.2641 (0.2604)	0.1102 (0.1122)	0.75 (0.75)
z	0.292 (0.304)	0.1049 (0.0937)	0.3650 (0.3807)	−0.0499 (−0.0486)

[a] Extended Hückel charges used (charge iteration applied). [b] Calculated values in parentheses.

Table 3 Results of energy minimizations for complex **5** in the correct space group *Pnma* and the subgroup $P112_1/a$



5

Parameter	Experimental[39]	Calculated crystal structure*	
Space group	*Pnma*	*Pnma*	$P112_1/a$
Z	8/2	8/2	4
a/Å	12.494	10.881	10.883
b/Å	9.503	9.725	9.724
c/Å	6.113	6.478	6.477
γ/°			90.002
U/Å^3	725.7	685.4	685.4
E_{vdW}/kJ mol^{-1}		−72.89	−72.90
E_{el}/kJ mol^{1}		−15.91	−15.68
E_{tot}/kJ mol^{-1}		−88.80	−88.58

* vdW and Coulombic interactions.

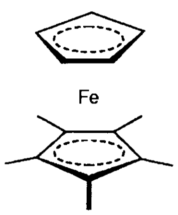
mirror plane. Only vdW and no Coulomb interactions were considered. The best results, *i.e.* the lowest lattice energy, were obtained for an eclipsed molecule in general position in $P\bar{1}$. Table 4 shows the good agreement between our prediction[40] and the experimentally established crystal structure.[41]

According to our experience, the choice of interaction parameters for non-peripheral atoms (like metals in most cases!) does not modify the order of precedence among different local minima of similar energy; it only slightly affects the agreement between calculated and experimental structures.

Unlike in the above example, the contribution of electrostatic interactions may not always be neglected. Though it is not easy to determine reliable charges for transition-metal complexes, Mulliken point charges from extended Hückel calculations with the charge-iteration procedure are at least a reasonable approximation. Table 5 shows the influence of vdW forces and electrostatic charges on the lattice energy of the ruthenium complex **7**. For this compound the following point charges resulted: Ru, +0.20; O, −0.18; C (carbonyl), +0.13; C of $C(CH_2)_3$, +0.03; C of $C(CH_2)_3$, 0.00; H, +0.01; dipole moment 6.6 × 10^{-30} C m. The charges stabilize the experimental $P\bar{1}$ structure with respect to alternative minima.

In all the above cases rigid molecules served as input for the minimization algorithm. How about 'soft' conformational degrees of freedom? In the relatively simple case of compound **6** the problem was solved by refining both rotamers separately. The energy difference for the free molecule is expected to be very low, and thus it was expected that the molecule will simply adopt the more favourable conformation for packing. Of course things are not necessarily as easy; in general, both intra- and inter-molecular forces may interfere, and the global minimum in terms of packing and conformation has to be found. In the field of organometallic compounds, internal degrees of freedom do not represent so much of a mathematical problem but require the availability of a sufficiently general intramolecular force field and its correct scaling *versus* the intermolecular parameters. General force fields for organometallic compounds are a current field of active research and far beyond the scope of this contribution. At the present state, organometallic molecules with many alternative conformational minima of similar energy must be considered as the limit of our method.

Table 4 Summary of experimental and calculated structures for pentamethyl ferrocene **6**

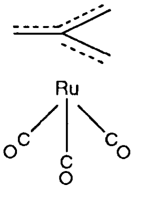


6

					$P2_1/m$			$P2_1/c$		*Pnma*	
Parameter	Exptl.	$P\bar{1}$ e	$P\bar{1}$ s	$P\bar{1}$ dis	e	s	$P1$ e	e	s	e	s
Z	2	2	2	4/2	2	2	1	4	4	4	4
a/Å	8.169	8.046	8.057	8.032	8.110	6.741	7.989	8.420	7.672	8.345	12.082
b/Å	12.239	11.889	12.962	12.171	12.153	13.128	6.801	10.899	13.000	11.889	8.653
c/Å	7.819	7.806	7.506	8.093	6.807	7.809	8.025	14.088	14.340	12.970	12.807
α/°	94.73	93.69	97.12	102.52			114.05				
β/°	117.81	118.23	120.81	120.18	99.16	107.39	114.95	94.76	112.69		
γ/°	73.14	73.28	72.85	75.26			67.39				
E/kJ mol^{-1}		−94.18	−89.85	−84.41	−86.61	−87.40	−80.61	−89.11	−86.16	−87.52	83.51

Exptl. = Experimental; e = eclipsed; s = staggered; dis = C_5Me_5 ring 1:1 disordered over an eclipsed and staggered arrangement with respect to C_5H_5.

Table 5 Summary of experimental and calculated crystal structures for $[Ru\{(CH_2)_3C\}(CO)_3]$ **7**



7

		Calculated crystal structures			
		Only vdW interactions		vdW and Coulombic interactions	
Parameter	Experimental structure[42]				
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$*	$P\bar{1}$	$P2_1/c$*
Z	2	2	4	2	4
a/Å	5.765	5.564	9.575	5.563	9.575
b/Å	7.096	7.006	6.196	7.071	6.146
c/Å	10.323	10.145	12.884	10.084	12.849
α/°	81.89	82.48		82.65	
β/°	84.46	83.44	90.12	83.32	90.20
γ/°	82.03	81.48		79.67	
Metal coordinates					
x	0.209	0.200	0.253	0.197	0.254
y	0.192	0.190	0.283	0.185	0.282
z	0.235	0.235	0.080	0.234	0.080
E/kJ mol^{-1}		−71.0	−72.6	−77.5	−77.5

* The minimization was performed in space group $P2_1/c$ but converged close to *Pnma* symmetry.

Conclusion

In the present contribution we have focused on crystal structure calculations. Though the prediction of possible crystal structures must be considered the most ambitious application of lattice-energy calculations and minimizations, the results obtained with our method are promising. The concepts and algorithms for probing the energy hypersurface by our extended atom–atom potential method are, however, not limited to the topic of structure prediction. Other applications include interpretation of dynamic phenomena[43] and disorder problems in molecular crystals[44,45] and will be the subject of forthcoming publications.

Acknowledgements

We thank Professor G. E. Herberich for fruitful discussions and his interest in this work. Helpful assistance from Dipl. Chem. Axel Koslowski and financial support from Deutsche Forschungsgemeinschaft and Studienstiftung des Deutschen Volkes (fellowship for M. U. S.) are gratefully acknowledged.

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Received 14*th August* 1995; *Paper* 5/05427C