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Investigation of the Si(111) $(\sqrt{3}\times\sqrt{3})R30^\circ$-Boron Surface Reconstruction by Simulated Annealing

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Abstract: In Monte Carlo and molecular dynamics simulations, millions of geometrical configurations are explored. A quick calculation of the energy of a many-body system is crucial. Of all the computational techniques in quantum chemistry, the extended Hückel method is one of the most economic. Although simplistic, it often gives valuable qualitative results in appropriately selected applications. It can be modified to give reasonable geometries of molecules. A combination of molecular dynamics and Monte Carlo simulations with the extended Hückel method should be useful in studying dynamic phenomena near surfaces and in the solid state. We have taken the first step by studying the reconstruction of the Si(111) $(\sqrt{3}\times\sqrt{3})R30^\circ$–boron surface structure using a modified extended Hückel method and Monte Carlo simulation. Our simulated annealing suggests that the reconstruction involves a three-atom rotation inside a silicon matrix instead of a direct exchange of the boron atom and the silicon atom under it.

Introduction

Computational algorithms and computer machinery have advanced to such a stage that simulations of dynamic phenomena of practical interest are feasible. Tremendous insight has been gained from these numerical experiments. Yet in certain sense, simulation science is still in its infancy. There is a lot of "art" in this rapidly expanding field. This makes things challenging, and it prevents computer simulation from degenerating into a routine. There is no substitute for excellent chemical and physical intuition. One of the goals of this work is to share the joy and pain of computer simulation with the reader.

The quest for the global minimum of a multidimensional function remains one of the most challenging and important issues in science and technology. The major breakthroughs in optimization occurred in the 1950s and 1960s. Yet for most cases of practical interest, the standard algorithms are only capable of determining the local minima. One frequently resorts to the brute-force approach in which the optimization procedure is executed for a large number of initial configurations, say N. As $N \rightarrow \infty$, the absolute minimum is located with certainty. In practice, N is always finite and the global minimum may remain illusive.

Simulated annealing, since its inception in 1982, has emerged as a promising tool in searching for the global minimum.[1,2] It has solved the classical traveling salesman problem (TSP), involving the determination of the shortest cyclic tour for a salesman to visit a large number of cities in turn. TSP is an NP-complete problem, that is, the cpu time to compute the exact solution scales exponentially with the number of cities. Other fruitful applications include the design of large-scale integrated circuits, image processing, code design, neutral network theory, refinement of X-ray crystallographic data, etc.[3–12]

Central in this method is nature's own mechanism of determining its most stable state. At thermal equilibrium, the probability of a system at an energy E above the ground state is characterized by the Boltzmann distribution function:

$$\rho(E) = \exp(-E/kT)/Z(T)$$

where $Z(T)$ is the partition function—a normalization factor depending on the temperature T— and k is the Boltzmann constant. Even at low temperatures, there is a finite probability of a system being in a high-energy state. Correspondingly, there is also a chance to escape from a local minimum in search of the global one. This process is often speeded up by annealing. A solid is heated to a high temperature and then cooled slowly. High temperature ensures a high probability of escape; heating provides more energy for the particles of a solid to overcome an activation barrier; slow cooling allows ample time for them to rearrange. In this way, strain and crystal imperfections are minimized. Strictly speaking, nature's global optimization as implemented by us may require an enormous amount of time. Yet all real and numerical experiments have to be completed within a reasonably short period. Trapping in a local minimum is still possible, and the process of annealing is frequently repeated several times in the laboratory, and so it has to be in numerical experiments as well.

In 1953, Metropolis translated these ideas into a numerical algorithm[13] which eventually formed the basis of the simulated annealing procedure proposed by Kirkpatrick.[14,15] Given a system of particles with an energy E_1, a new configuration is generated by displacing each particle by a random amount. The energy of the new configuration E_2 is computed. If the new configuration is more stable than the old one, $E_1 > E_2$, the random perturbation is continued with the new state. If $\Delta E = E_2 - E_1 > 0$, the new configuration is accepted with a probability given by the Boltzmann factor, $\exp(\Delta E/kT)$. If the new state is rejected, the random perturbations are repeated on the old configuration. Following this Metropolis criterion, the system eventually evolves into thermal equilibrium. The sequence of configurations generated in this process defines a Markov chain. The length of this chain, L, is in turn characterized by the number of successful transitions. The temperature is then reduced in step, typically by a factor of 0.75–0.90. For reach step, the Markov chain should be long enough to allow the system to approach equilibrium. Provided L is large enough and the decrement in temperature for each step is small (the essence of slow cooling), the system attains its ground state at low temperature. The final solution obtained by simulated annealing should not depend on the initial configuration. However, this method is computationally much more intensive than ordinary

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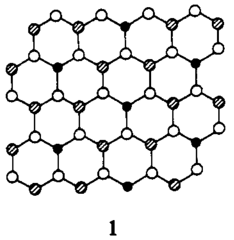
iterative algorithms. In actual simulations, it has been found that, after cooling to a reasonably low temperature, switching to a conventional minimization algorithm such as the steepest descent method leads to a great reduction in computational time.[1,2] It is also common practice to absorb the Boltzmann constant k into the temperature and write the Boltzmann factor as $\exp(-\Delta E/T)$. Now the temperature T has the dimension of energy. In the field of combinatorial optimization, the Boltzmann factor is usually written as $\exp(-E/C)$ where E is the cost function and C is the control parameter.

Surface reactions and solid-state reactions are of utmost technological importance. They are of direct relevance to catalysis and corrosion. Although a full quantum mechanical treatment of these processes is usually impossible, simulations of biochemical phenomena in the past two decades have proven that semiempirical and even empirical approaches often give valuable information.[16,17]

The extended Hückel method has been providing valuable insight into bonding in discrete molecules and solid-state compounds.[18,21] It is also useful for elucidating adsorbate–surface interactions.[22] This approximate molecular orbital calculation is transparent and economic. The main drawback is its incapability of predicting bond length reliably. A new version of this method, recently proposed by Calzaferri, seems to be able to predict molecular geometry accurately.[23] The main features of this method are a distance-dependent k and the inclusion of two-body repulsions. (The two-body electrostatic interactions were originally derived by applying the Hellmann–Feynman theorem. Notice that Calzaferri's version is actually a variant of the atom superposition and electron delocalization (ASED-MO) technique first put forward by Anderson.[24]) By combining simulated annealing with the improved extended Hückel calculations, we hope to provide some interesting results. The parametrization is specified in the Appendix; the reader is referred to Calzaferri's paper[23] for calibrations of the method.

For a starter, we try to optimize the bond length of H_2 by simulated annealing. The computed bond length is 0.77 Å. The experimental value is 0.74 Å. For methane (CH_4), the initial C–H bond and H–C–H angle are arbitrarily set to 1.60 Å and 90°, respectively. The optimized bond length and bond angle are 1.19 Å and 109.5°, compared to the experimental values of 1.10 Å and 109.5°, respectively. In other words, the tetrahedral geometry has been regenerated from a square-planar configuration, but the calculated C–H distances are long.

Stimulated by these encouraging results, we incorporated the above two features into our band programs. The first case we would like to study is the adsorption of a boron atom on the Si(111) surface. Due to its promising technological properties, this system has been the subject of intensive investigation recently.[25-30] The experimental probes applied include scanning tunneling microscopy (STM), low-energy electron diffraction (LEED), and synchrotron X-ray diffraction, while the density functional calculation is the major theoretical tool. At low temperatures, the boron adatom sits on top of a second-layer silicon atom and is bonded to three other silicon atoms of the top layer, as indicated in the top view **1**. (The empty, dashed and solid circles represent the top-layer silicon atoms, second-layer silicon atoms, and the adsorbate, respectively.) The coordination number of the adsorbate is thus 4, and this adsorption site is called the T_4 site, **2**. Note the unusual, propellane-like bonding situation. This mode of adsorption gives rise to a $(\sqrt{3}\times\sqrt{3})R30°$ LEED pattern. On annealing (now real, not in the computer!) at 1000 °C, the boron atom substitutes for a second-layer silicon atom. The T_4 site is in turn occupied by a silicon atom. The new silicon adatom is directly over the boron atom, **3**. Now the boron atom is bonded to five silicon atoms and is located at the S_5 site (S for substitution). This is the first well-established case for subsurface substitutional doping of a semiconductor. It is also a unique situation where atoms originally adsorbed on top of a surface are finally embedded under two layers of the host material. Introduction of point defects in this surface structure leads to negative differential resistance (NDR) behavior, that is, a decrease in electric current with increasing voltage. NDR is the crucial property that allows devices to be used as fast switches, oscillators, and frequency locking circuits.[31,32] Notice that, in the famous Si(111) 7×7 reconstruction, the silicon adatoms are also located at the T_4 sites. Finally, the whole process involves breaking and reforming of many Si–B and Si–Si bonds. The typical bond energy for a covalent single bond is of the order of 4 eV. Hence, the establishment of the mechanism of reconstruction would be a real challenge. Since simulated annealing is basically a computer simulation of the physical annealing procedure, this method should be ideal for this purpose.



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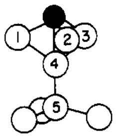

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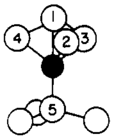

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It is appropriate to mention explicitly at this point that there is much other theoretical work in the literature on the simulation of surfaces, often carried out using tight-binding or density functional methods. In particular such methods have been applied recently to the Si(111) surface[33] as well as other systems.[34]

Model for the Si(111) Surface

Silicon adopts the diamond structure. Its face-centered cubic (fcc) unit cell consists of a two-point basis at 0,0,0 and $^1/_4,^1/_4/^1/_4$. In other words, the silicon structure is made up of two interpenetrating fcc lattices displaced relative to each other along the body diagonal of the cubic unit cell by one-quarter of the length of the diagonal. Every silicon atom is tetrahedrally coordinated. The nearest-neighbor distance is 2.35 Å. The hexagonal (111) surface is the close-packed plane. In the unreconstructed surface, there is one dangling bond for every (1×1) surface unit cell. There are in turn three dangling bonds in the Si(111) $(\sqrt{3}\times\sqrt{3})R30°$ unit cell. The three dangling bonds can be eliminated by putting

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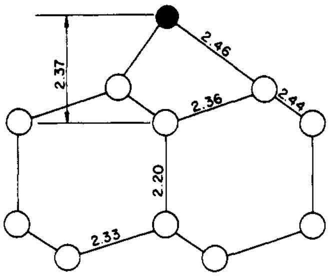
a boron atom at the T_4 site. Since the covalent radius of boron (0.90 Å) is much smaller than that of silicon (1.18 Å), adsorption of the former at the T_4 site would indice a substantial amount of stress at the silicon surface. In fact, assuming a completely undistorted Si(111) surface and putting the boron atom at the T_4 site such that it is 2.4 Å from the three top-layer silicon atoms, the distance between the boron atom and the fourth silicon atom would be about 1.6 Å. This is quite short, though such separations are found in [1.1.1]propellane.[35,36] Relief of surface strain has been proposed to be the main reason for the instability of the T_4 site relative to the S_5 site.[25-27] Nevertheless, the boron atom is five-coordinated at the S_5 site. This may introduce even more strain into the silicon lattice. We thus have some reservation about the above proposal.

In a compromise between speed and accuracy, the Si(111) surface is modeled by a five-layer slab of atoms. The boron atoms are put on one side of the two-dimensional slab only. In all calculations, the ($\sqrt{3}\times\sqrt{3}$)*R*30° unit cell is preserved.

Although the exact geometry of the T_4 site is unknown, some useful information is available. When the boron atom occupies the S_5 site, only its five nearest neighbors labeled in **3** show significant displacements from their original positions. The other silicon atoms are essentially stationary. For aluminum and gallium adsorbed at the T_4 site of Si(111), the LEED patterns are compatible with a C_{3v} point group symmetry.[37,38] The same is true for boron at the S_5 site. We therefore optimized the positions of the boron atom and the five silicon atoms labeled in **2** by imposing C_{3v} symmetry. The symmetry constraint reduces the number of variables from eighteen (3×6) to five. The optimized geometry is sketched in **4**, which also serves as the initial configuration for our computer simulation. The C_3 axis is perpendicular to the surface, passing through the adsorbate. Notice that only the optimized bond lengths are given. All the other Si–Si bonds are fixed at 2.35 Å. To get a rough idea of the accuracy of our optimization, we repeat the minimization procedure for the case of aluminum and gallium. The computed bond lengths are compared with the experimental findings (in parentheses) in **5** and **6**. The experimental error is about 0.1–0.2 Å. The relatively large error is perhaps enough to convince the reader that determination of bond lengths at the surface is extremely difficult. Despite many years of intensive research, no surface structural tools can give results as reliable as X-ray diffraction for single crystals. The *R* (agreement) factor for LEED is unusually higher than 15%.[29,37-39] Yet, dynamical LEED is already one of the most flexible and reliable probes currently available for complicated surface structure. As far as the theory goes, a complete geometry optimization or an increase in the thickness of the silicon slab may improve the computed bond lengths. (It is not uncommon to use a slab of 10 layers or more to model the Si(111) surface.) However, the focus of this work is surface dynamics, not the statics. We do not intend to invest an excessive amount of computational time on the latter.



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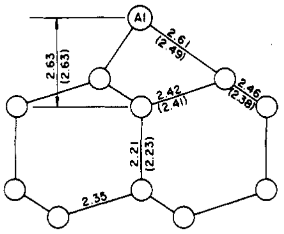

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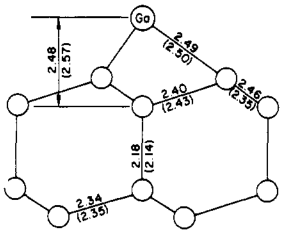

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The silicon slab, together with the boron atom at the T_4 site, is then annealed in the vacuum; that is, there is no boundary in the *z* direction and the silicon slab is periodically extended in the *x* and *y* directions. The coordinates of the boron atom and the labeled silicon atoms in **2** are varied simultaneously and randomly. The positions of other atoms are fixed. One obvious danger of this procedure is that some of the atoms may leave the slab and vaporize into the vacuum. Fortunately, this is not likely if the Markov chain is long enough. Since our initial geometry corresponds to a local minimum, all standard optimization algorithms will fail to effect the transformation from the T_4 site to the S_5 site. Simulated annealing is the only option available.

Implementation of Simulated Annealing

To specify a cooling schedule in simulated annealing, four parameters have to be defined: (a) the initial temperature, (b) the final temperature, (c) the length of the Markov chain, and (d) the cooling factor. It is perhaps fair to state that a universal, efficient cooling schedule for global minimization has not yet appeared.

The choice of initial temperature T_0 is probably the most important part of simulated annealing. If T_0 is too high, the system will not feel the attraction to the global minimum. Essentially, it just wanders randomly on the potential energy surface. An excessively small T_0, however, would lead to trapping in a local minimum. To ensure a fast approach to equilibrium, Kirkpatrick et al. suggested that T_0 and the initial step size should be chosen such that no less than 80% of the transitions are accepted.[14] A much lower accepted probability (25–50%), however, seems to be sufficient for the Lennard-Jones or the Coulomb potential.[1,2] The rule of thumb for Metropolis sampling is that the rejection ratio should be about 50%. Yet there is a claim that an acceptance ratio of 10% is most cost-efficient.[40]

In view of these controversies, we rely on our chemical intuition. The *experimental* annealing temperature is around 1000 °C. An educated guess of the activation energy of the reconstruction would be 1–2 eV. A value of 2.5 eV for T_0 should be sufficient. From the molecular simulations mentioned previously, we discovered that an acceptance ratio as high as 66% seems to work well. We therefore adjust our step size to attain this ratio. The initial step size turns out to be 0.12 Å.

Typically, for a many-body system in which the coordinates of *X* atoms are varied simultaneously, the rule of thumb is to perform 100*X* trial moves for every temperature.[1,2] This is currently beyond our computational capability, because it takes about 36 h of cpu time on a Sun4 workstation to complete a calculation for 600 configurations. Research on the traveling salesman problem (TSP) indicates that instead of fixing the number of trial moves for each temperatur, it may be more meaningful to focus on the number of successful transitions, that is, the length of the Markov chain *L*. Indeed there is an existing algorithm for the TSP, setting *L* to 10*N* where *N* is the number of cities.[41] In our case 18 atomic coordinates are varied simultaneously and randomly. Thus, *L* corresponds to 180. There

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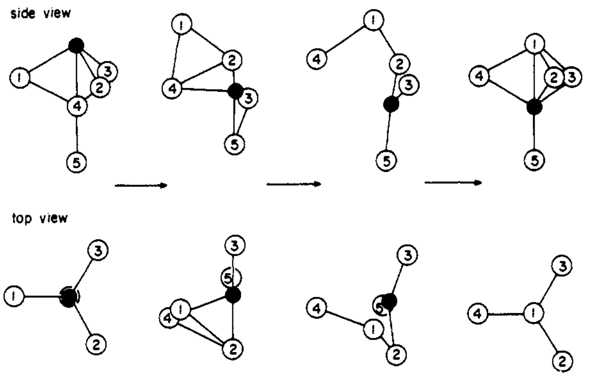


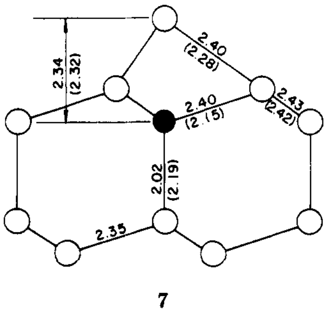
Figure 1. Positions of the boron atom and the other five silicon atoms in the course of our Monte Carlo simulation.

is still too computationally intensive for us, so we reduce L to 120. Preliminary simulations suggested that there is a tendency for the silicon atoms to vaporize into the vacuum if L is less than 120.

The cooling factor is chosen to be 0.875. If we perform the simulated annealing for 50 cycles, the final temperature would be 3.6 meV. This temperature should be low enough for all practical purposes. (25 meV is roughly equivalent to 300 K.) This, however, also corresponds to about 24 days of cpu time on the above-named system. Fortunately, after the second cycle, the boron atom has shifted downward over a distance of 1.6 Å and bonds to a third-layer silicon atom. One of the top-layer silicon atoms has moved up by about 2.3 Å and become an adatom. The adatom in turn bonds to two other silicon atoms below to form a bridge trapping the boron atom within the silicon matrix. The silicon atom in the second layer, which was initially 2.3 Å under the boron atom, now shifts above the latter and bonds to the adatom. The major activation barrier may have been overcome, and there may be no need to maintain the system at such a high temperature. Thus, after the second cycle, we anneal the whole system at a temperature between 0.5 and 0.2 eV for nine more cycles.

At the end of the 11th cycle, we obtain all the essential features of the surface reconstruction. The boron atom has shifted downward to the second layer; the silicon lattice starts to reform. Hence, we set the temperature to zero and continue the random search for the minimum. (Actually we have performed the annealing process for one more cycle, that is, about 10 h more of cpu time. However, there is little improvement in the convergence of energy in the 12th cycle. That is another reason for quenching the system.) At the end of our simulation, the C_{3v} symmetry is regenerated within an error of 0.016 Å in the atomic coordinates. The boron atom has settled down at the S_5 site. The S_5 site is computed to be more stable than the T_4 site by about 2.5 eV. The same minima were reached with two alternative initial configurations, and using different annealing schedules.

In 7, we compare the computed bond lengths in the final configuration of our computer simulation with the experimental findings obtained by LEED (R factor 24.4%).[30] Since there is a slight deviation from the exact C_{3v} symmetry, the computed bond lengths listed in this figure are the averages over the three bonds supposed to be symmetry-equivalent. In Figure 1, we sketch the initial configuration, the final configuration at the second cycle, the final configuration at the eleventh cycle, and the configuration at the end of our simulation. For clarity, only the top and side views of the six atoms whose positions are varied are shown. Two atoms are connected by a line if their separation is less than 2.85 Å.



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In summary, our computer simulation suggests that the reconstruction involves a three-atom rotation inside a silicon matrix instead of a simple exchange of positions between two atoms. Each of the three atoms moves over a distance of more than 2.3 Å. Hence, on the extended Hückel potential energy surface, the local minimum corresponding to the T_4 site is really far from the deeper minimum of the S_5 site. Apart from our limited computing resources which confine us to optimize at most 18 atomic coordinates, and the imposed translational symmetry (an intrinsic restriction of our band programs), our search for the reaction pathway is otherwise unbiased. There is no additional assumption concerning the mechanism of the surface reconstruction. The second constraint mentioned may not be as severe as it seems, because experimentally it has been found that the ($\sqrt{3}\times\sqrt{3}$) unit cell is preserved when a boron atom is located at the T_4 and the S_5 site. We hope that our proposed mechanism will be tested in the near future by isotopic labeling. To our knowledge, this is the first study of surface reconstruction by simulated annealing. There is, however, a recent study of a simpler surface reconstruction by molecular dynamics.[34]

Density functional theory (DFT) is ideal for extended systems and large molecules.[42,43] Although computationally intensive, it tends to give excellent results, especially for free-electron systems. Incidentally, our tight-binding calculations are most likely to fail in such systems. Central to DFT is that the ground-state energy is a unique functional of the electron density. Once this functional can be determined exactly, there is no need for any iteration in density functional calculations. The gain in cpu time would be enormous. Given the intensive research devoted to this subject, analytically by the coordinate scaling[44,45] and numerically by quantum Monte Carlo simulations,[46] this goal may be achieved, at least partially, in the near future.

We believe that simulated annealing, together with molecular dynamics and density functional theory, will become the main tool for investigating surface dynamics, such as the formation and reactivity of the Si(111) 7×7 reconstruction, catalytic reactions such as the Fischer–Tropsch reaction, or corrosion processes such as the interaction of oxygen and water with metal and semiconductor surfaces. Simulated annealing can also be applied to study dynamic phenomena in the solid state, such as the diffusion of oxygen in high T_c superconductors. The experimental activation energy for oxygen diffusion in $YBa_2Cu_3O_7$ is about 0.4 eV. Another possibility would be the elucidation of the mechanism for the formation of C_{60}. The applications of computer simulation are open-ended. One of the focuses of our future research will be to combine density functional theory and computer simulation to study dynamic processes in condensed phases, and the mechanisms for the formation of clusters such as C_{60}, C_{70}, Al_6, and Fe_{13}.

Conclusion

We have investigated the mechanism of the Si(111) ($\sqrt{3}\times\sqrt{3}$) *R30°*–boron surface reconstruction by simulated annealing, using a modified extended Hückel method. Our rough computations suggest that the reconstruction involves a three-atom rotation inside a silicon matrix, as shown in Figure 1. Due to our limited computing resources, we had to impose some constraints in the search for the reaction pathway. The dynamic aspects of surface phenomena are very difficult to study either theoretically or exper-

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Table I. Extended Hückel Parameters

atom	orbital	H_{ii} (eV)	ζ
H	1s	−13.6	1.30
C	2s	−21.4	1.63
	2p	−11.4	1.63
Si	3s	−17.3	1.38
	3p	−9.2	1.38
B	2s	−15.2	1.30
	2p	−8.5	1.30
Al	3s	−12.3	1.17
	3p	−6.5	1.17
Ga	4s	−14.5	1.77
	4p	−7.8	1.55

imentally. We would be more than rewarded if this work can stimulate further research in that direction.

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Appendix

All calculations are performed by the extended Hückel method within the tight-binding formalism.[18,19,47,48] The distance-dependent k

$$k = 1 + (\kappa + \Delta^2 - \Delta^4\kappa)\exp(-\delta(r - d_0))$$

$$\kappa = 0.80 \qquad \Delta = (H_{ii} - H_{jj})/(H_{ii} + H_{jj}) \qquad \delta = 0.13$$

and the two-body repulsions have been explained in a previous paper.[23] The extended Hückel parameters are listed in Table I. The k points are generated according to the geometrical method of Böhm and Ramirez.[49]

Registry No. Si, 7440-21-3; B, 7440-42-8.

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Electron Distributions in Peptides and Related Molecules. 2. An Experimental and Theoretical Study of (*Z*)-*N*-Acetyl-α,β-dehydrophenylalanine Methylamide

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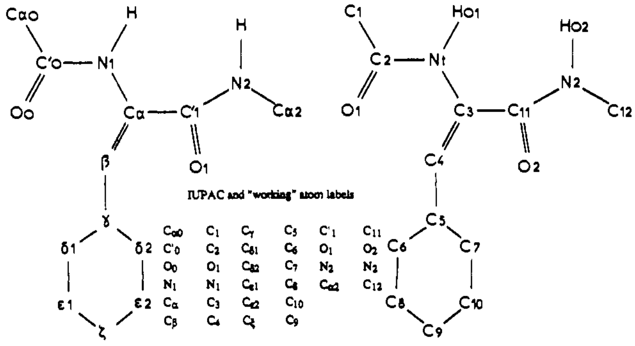
Abstract: The crystal structure, thermal vibrations, and electron density of (*Z*)-*N*-acetyl-α,β-dehydrophenylalanine methylamide have been analyzed using single-crystal X-ray diffraction data measured at 100 K with Mo Kα radiation to a resolution corresponding to $(\sin\theta_{max})/\lambda = 1.35$ Å^{-1}. Averaging equivalent data among the 14666 reflections measured gave 7324 unique data [$R_1(F^2) = 0.016$]. A multipolar atomic density model was fitted against the 6035 unique data with $I > 3\sigma(I)$ [$R(F) = 0.022$, $R_w(F) = 0.018$] in order to calculate phases for the crystal structure factors and map the valence electron distribution. Ab initio SCF calculations have been carried out at the crystallographic molecular geometry with two basis sets. The density maps obtained with a medium-size basis set (double-ζ quality for the valence shell of all atoms) agree qualitatively with the experimental static model maps. Near quantitative agreement between theory and experiment is obtained with an extended basis set (triple-ζ plus polarization quality for the valence shell of all atoms, except those belonging to the methyl and phenyl substituents). Crystal data: $C_{12}H_{14}O_2N_2$, $M_r = 218.32$; monoclinic *Cc* from 295 to 100 K; at 100 K $a = 10.193$ (1), $b = 15.115$ (1), and $c = 8.561$ (2) Å, $\beta = 121.13$ (2)°, $V = 1129$ Å^3, $Z = 4$, $\rho_x = 1.28$ g cm^{-3}, μ(Mo Kα) $= 0.9$ cm^{-1}, $F(000) = 464$ electrons.

Introduction

The proper description of electrostatic properties of small peptides and pseudopeptides is of considerable importance for our understanding of molecular recognition processes and for the design of new drugs. As part of our program[1,2] to map the electron distribution and to calculate the electrostatic properties of peptides we have already studied *N*-acetyl-L-tryptophan methylamide[3] and Leu-enkephalin, for which a preliminary report has been published.[4] In our study of *N*-acetyl-L-tryptophan methylamide[3] we have obtained a reasonable agreement between experimental and theoretical deformation density maps, within the limitations im-

Chart I



IUPAC and "working" atom labels

$C_{\alpha 0}$	C_1	C_γ	C_5	C'_1	C_{11}
C'_0	C_2	$C_{\delta 1}$	C_6	O_1	O_2
O_0	O_1	$C_{\delta 2}$	C_7	N_2	N_2
N_1	N_1	$C_{\varepsilon 1}$	C_8	$C_{\alpha 2}$	C_{12}
C_α	C_3	$C_{\varepsilon 2}$	C_{10}		
C_β	C_4	C_ζ	C_9		

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