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Lattice energy of some organic molecular crystals

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Abstract : Lattice energies of the crystals of biphenyl and pyracene have been calculated using MKB and William sets of 6-exponential non-bonded potential parameters. The comparison of the calculated values of lattice energy with the corresponding values of heat of sublimation shows that MKB set is more suitable than the William set of parameters. The proposed potential parameters for urea take care of hydrogen bond energy in the form of van der Waals interaction energy and give accurate values of lattice energy, lattice parameter and conformation energy.

Keywords : Non-bonded interatomic potential, lattice energy, organic molecular crystals

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The structure and properties of Organic Molecular Crystals can be calculated using suitable non-bonded interaction potential parameters. The interaction potential between two non-bonded atoms separated by distance r is given by the equation

$$\Phi = -Ar^{-6} + Be^{-\alpha r},$$

where A, B and α are potential parameters. The lattice energy is the sum of the interaction potential energies of all atoms of the reference molecule with all atoms of the surrounding molecules. The space group symmetry operation is performed on the reference molecule to generate the surrounding molecules. The summation is continued till the lattice energy attains a constant value. The straight forward method of selecting suitable parameters is to calculate lattice energy and compare it with the experimental value of heat of sublimation. Mirskaya, Kozlova and Bereznitskaya [1] abbreviated as MKB obtained potential parameters for C$\cdots$C, C$\cdots$H and H$\cdots$H interactions using the structure and heat of sublimation data and latest elasticity data of the crystals of benzene, naphthalene and anthracene all extrapolated to absolute zero where the effects of molecular and lattice vibrations are minimised and the crystal properties are mainly determined by the interaction potential energy. Mirasky [2] used these parameters to calculate lattice parameter, lattice energy of the crystals of methane, 2,2-paracyclophane and 3,3-paracyclophane. The calculated values agreed satisfactorily with the experimental values. He also studied successfully the solid phase transition peculiarity of adamantane crystals. William [3] obtained these parameters using the structure data of 18 hydrocarbon crystals half of them aromatic and half saturated hydrocarbons and the heat of sublimation of benzene and naphthalene reduced to absolute zero. The steepness of the corresponding curves is the same but the coordinates of minima differ slightly. Trotter [4] reported that the crystals of biphenyl are monoclinic of space group $P2_1/a$. There are two molecules per unit cell of dimension $a = 8.12$ Å, $b = 5.64$ Å, $c = 9.47$ Å and $\beta = 95.4°$. Simmons and Lingafelter [5] showed that pyracene crystals are monoclinic of space group $P2_1/n$ containing two molecules per unit cell of dimensions $a = 12.56$ Å, $b = 5.64$ Å, $c = 7.32$ Å and $\beta = 95°14'$. Natalie *et al* [6] found that urea crystals are tetragonal of space group $P\bar{4}2_1$, m. There are two molecules in the unit cell of dimensions $a = 5.662$ Å and $c = 4.71$ Å. The molecules are planar and linked to each other through N — H ··· O bonds in the crystal structure. The calculation of lattice energy of urea is interesting because the crystal is of chemical importance and lattice energy consists of van der Waals interaction energy and hydrogen bond energy. In urea, there are N···N, O···O, O···N, C···O, C···N, O···H, N···H interactions in addition to C···C, C···H and H···H interactions. The parameters of Dashevsky [7] for N···N and O···O interactions were combined with MKB set of parameters for C···C and H···H interactions to deduce parameters for the above interactions according to the formula

$$A_{12} = (A_{11}A_{22})^{1/2},\ B_{12} = (B_{11}B_{22})^{1/2} \text{ and } \alpha_{12} = 1/2(\alpha_{11} + \alpha_{22})$$

When these parameters were used to calculate the lattice energy of urea, low value was obtained because they were not taking care of hydrogen bond energy As the depth of the interaction potential is responsible for the lattice energy, it became essential to increase the A values of all interactions. According to Pauling and Wilson [8], the van der Waals interaction energy between two atoms 1 and 2 separated by distance r is given by the equation

$$W = -6\left(n_1 n_2 Z_1^{\bar{2}} Z_2^{\bar{2}} e^4 r^{-6}\right)/(I_1 + I_2),$$

Therefore $$A = \left(6n_1 n_2 Z_1^{\bar{2}} Z_2^{\bar{2}} e^4\right)/(I_1 + I_2),$$

where n_1 and n_2 are effective number of electrons, I_1 and I_2 are the first ionisation energies, e the charge of an electron, $Z_1^{\bar{2}}$, $Z_2^{\bar{2}}$ are the average of the square of the coordinates of the electrons in the field direction relative to the nuclues. Thus, A is proportional to the product of the effective number of electrons. In H···H interaction, this product is unity. Therefore, A for H···H interaction becomes constant of proportionality. In MKB set, it is 29 whereas it is 40.2 in William set. The average of these two is 35 which has been taken as A value for H···H. As the effective number of electrons in carbon, nitrogen and oxygen atoms are 4, 5 and 6, the A values for C····C, N····N and O····O interactions become 560, 875 and 1260 respectively. The Dashevsky's values of B and α for N····N — O····O interactions were so adjusted that the interaction energy attains minimum value at observed crystallographic distances. The potential parameters obtained according to above combination rules are given in Table 1.

Table 1. Potential parameters.

Atom pair	A (K cal A^6/mole)	B (K cal/mole)	α (Å^{-1})
C····C	560	7.16×10^4	3.68
C····H	140	1.86×10^4	3.94
H····H	35	0.49×10^4	4.29
N····N	875	7.62×10^4	4.06
O····O	1260	9.69×10^4	4.09
O····N	1050	8.59×10^4	4.09
C····O	840	8.33×10^4	3.69
C····N	700	7.39×10^4	3.87
O····H	210	2.18×10^4	4.34
N····H	175	1.93×10^4	4.18

The calculated values of lattice energy, the heat of sublimtion and the chemical formula of the crystals are given in Table 2.

Table 2. Chemical formula and lattice parameters.

Name of crystal	Chemical formula	U (K cal/mole)	H_0 (K cal/mole)
Biphenyl	$C_{12}H_{10}$	19.6	19.5
Pyracene	$C_{14}H_{12}$	20.7	20.7
Urea	CON_2H_4	20.92	21

As the charge distribution of the overlapping electron cloud of two atoms responsible for the repulsive force is represented by the exponential density function, the 6-exponential potential is more accurate than the 6–12 potential. The lattice energy is minimum at 4.68 Å which is close to $c = 4.71$ Å. The non-bonded part of the conformation energy on the basis of the proposed parameters is −1.9 K cal/mole.

The lattice energies of biphenyl and pyracene obtained on the basis of William set of parameters are 16.8 and 17.34 K cal/mole. This shows that the MKB set is more suitable than the William set of parameters.

Recently, Wendy *et al* [9] proposed force field for the simulation of proteins, nuclic acids and organic molecules. On the basis of that force field, the C····C, N····N and O····O contributions to lattice energy of urea are −0.283, −0.228 and −1.934 K cal/mole which are greater than the corresponding values -0.338, -0.797 and -3.281 K cal/mole obtained on the basis of the proposed parameters.

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