

Theoretical Calculation of the Crystal Structures of Tetraphenyl Compounds of Methane, Silicon, Tin and Lead

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The molecular and crystal structures of $C(C_6H_5)_4$, $Si(C_6H_5)_4$, $Sn(C_6H_5)_4$ and $Pb(C_6H_5)_4$ have been determined by conformational analyses and lattice energy calculations. The molecular conformations and crystal structures correspond to the potential energy minima. The structure of $Sn(C_6H_5)_4$ is in good agreement with that determined experimentally by the X-ray method.

Introduction

The compounds $C(C_6H_5)_4$, $Si(C_6H_5)_4$, $Sn(C_6H_5)_4$ and $Pb(C_6H_5)_4$ were studied as part of a programme of theoretical determination of some simple structures (by conformational analysis and lattice energy calculations) in which the theoretical structures were compared with experimental results obtained from X-ray analysis. The calculation of the conformation of a molecule amounts to the determination of the structure having the minimum potential energy. A mechanical model of a molecule has often been used successfully in conformational calculations (Kitaigorodsky, 1960; Kitaigorodsky & Dashevsky, 1968). The method of atom-atom potentials has previously been used to calculate the lattice potential energy surface of several structures. Good agreement was found between structures corresponding to the minimum energy and the experimental results (Kitaigorodsky, Mirskaya & Tovbis, 1968; Mirskaya & Kozlova, 1969).

An X-ray study of the structures of $Si(C_6H_5)_4$, $Sn(C_6H_5)_4$ and $Pb(C_6H_5)_4$ was carried out by Ždanov & Ismailzade (1949, 1950) and of $C(C_6H_5)_4$ by Sumsion & McLachlan (1950). It was found that these compounds crystallize in the tetragonal system. The space group is $P4_21c$ which has eight equivalent positions. As there are two molecules per unit cell, the central atoms of the molecules must occupy special positions

000 and $\frac{111}{222}$, while the atoms of the phenyl groups are in general positions with the restriction that the molecule has $\bar{4}$ symmetry. If it is assumed that the central atom of the molecule is tetrahedrally surrounded by the four phenyl groups, and the values of the lattice parameters are fixed, then the structure can be described in terms of two parameters: the angle of rotation θ of the phenyl groups about the tetragonal bonds of the central atom, and the angle of rotation φ of the entire molecule about the $\bar{4}$ axis, *i.e.* the z axis of the crystal. Values of θ and φ obtained from consideration of the intensities of some reflexions, as described by the above authors, are shown in Table 1. The angle θ is measured from a vertical plane through z , and the angle φ is measured horizontally from the yz plane.

Table 1. *Structural parameters*

| Compound | θ | φ | a | c |
|----------------|----------|-----------|---------|--------|
| $C(C_6H_5)_4$ | 35 | 7.5 | 10.87 Å | 7.23 Å |
| $Si(C_6H_5)_4$ | 37 | 8.0 | 11.30 | 7.05 |
| $Sn(C_6H_5)_4$ | 42 | 8.0 | 11.85 | 6.65 |
| $Pb(C_6H_5)_4$ | 50 | 5.5 | 12.05 | 6.55 |

Conformational analysis

If the deformation of the tetrahedral angles at the central atom and the deformation of valence bonds are not considered the conformation of the molecule is determined solely by the minimum of the interaction energy U , between all non-bonded pairs of atoms:

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Table 2. *Interaction curve data*

| | A (kcal.mole ⁻¹) | B (kcal.mole ⁻¹ × 10 ⁴) | α |
|-----------|-----------------------------------|---|----------------------|
| Si ··· Si | 1160 | 4.2 | 2.95 Å ⁻¹ |
| Si ··· C | 662 | 4.2 | 3.23 |
| Si ··· H | 311 | 4.2 | 3.67 |
| Sn ··· Sn | 1401 | 4.2 | 2.85 |
| Sn ··· C | 732 | 4.2 | 3.18 |
| Sn ··· H | 347 | 4.2 | 3.60 |
| Pb ··· Pb | 912 | 4.2 | 3.06 |
| Pb ··· C | 582 | 4.2 | 3.30 |
| Pb ··· H | 268 | 4.2 | 3.81 |

$$U = \sum_{ks} f(r_{ks}), \quad (1)$$

where f is the interaction of non-bonded atoms k and s and r_{ks} is their distance apart.

The interaction potential f is given by:

$$f(r) = -Ar^{-6} + B \exp(-\alpha r). \quad (2)$$

The values of A , B , and α for C...C, C...H and H...H interactions have been given by Kitaigorodsky (1966). The interactions between the central atom of the molecule and the C and H atoms of the phenyl groups were not included in the summation, as they are constant for all values of θ . The bond lengths used are those found in other similar compounds, the C-C phenyl bond length was taken as 1.39 Å and the C-H length as 1.08 Å. The distances between the central atom and the C atom of the phenyl group were taken as: C-C=1.50, Si-C=1.84, Sn-C=2.14 and Pb-C=2.29 Å.

The potential energy of each molecule was calculated from $\theta=0$ to $\theta=90^\circ$ at intervals of 5° . Fig. 1 shows the relation between U and θ for the four compounds. The depths of the minima are 18, 3, 1 and 0.5 kcal.mole⁻¹ for C(C₆H₅)₄, Si(C₆H₅)₄, Sn(C₆H₅)₄ and Pb(C₆H₅)₄ respectively. The curve becomes flatter as the distance between the phenyl groups and the central atom increases. In other words the possible range of rotation of the phenyl groups increases as their distance from the central atom increases. For the molecules of Si(C₆H₅)₄, Sn(C₆H₅)₄ and Pb(C₆H₅)₄, because the value of $dU/d\theta$ is small the free molecule may be sensitive to any external lattice field. In this case the structure of the molecule in the crystal may be influenced by intermolecular interactions in addition to intramolecular interactions.

Conformations of the molecules in the crystals

If the summation of equation (1) is performed over both inter- and intramolecular distances between non-bonded atoms we get a quantity U_T which is the sum of the potential energy of the molecule and the lattice energy of the crystal. In our case U_T is a function of θ , φ and the lattice parameters. The unit-cell dimensions shown in Table 1 were used except for Sn(C₆H₅)₄ for which the new values $a=11.970$ and $c=6.604$ Å (Ahmed & Alexandrov, 1970), were taken. Calculations of U_T were performed at 5° intervals for values of θ and φ varying from 0 to 90° . For the intermolecular interactions between atoms other than carbon and hydrogen, the interaction curves were obtained by substituting the corresponding values of r_0 in the universal formula:

$$U = -\frac{0.119r_0^6}{r^6} + 4.2 \times 10^4 \exp\left(-\frac{13.6}{r_0} r\right)$$

(Kitaigorodsky & Mirskaya, 1964). r_0 was taken as the sum of the van der Waals radii, obtained from X-ray crystal structure analyses, of the two interacting

atoms, increased by approximately 10%. The values of the van der Waals radii used for Si, Sn and Pb were 2.10, 2.17 and 2.02 Å respectively (Bondi, 1964). Table 2 gives the data for the interaction curves used.

Maps giving the variation of U_T with θ and φ are shown in Fig. 2; contours are at 10 kcal.mole⁻¹ intervals and contours of high values were omitted. Table 3 shows the values of θ and φ corresponding to the minima in the maps.

Table 3. *Minima values of θ and φ*

| Compound | θ | φ |
|---|----------|-----------|
| C(C ₆ H ₅) ₄ | 44 | 7.5 |
| Si(C ₆ H ₅) ₄ | 51 | 7.5 |
| Sn(C ₆ H ₅) ₄ | 59 | 7.0 |
| Pb(C ₆ H ₅) ₄ | 62 | 5.5 |

It should be pointed out that any variations in the interaction curves used (Table 2) do not affect the positions of the minima as the interactions of the central atom with other atoms are approximately constant and of low value. The angles $\theta=59^\circ$ and $\varphi=7^\circ$ for Sn(C₆H₅)₄ are in good agreement with the experimental values $\theta=57^\circ$ and $\varphi=7^\circ$ determined by the X-ray method (Ahmed & Alexandrov, 1970). The values of θ and φ derived from the maps depend on the lattice parameters used, and redetermination of these parameters may have a small effect on these values. Recently a report of another X-ray determination of the structure of Sn(C₆H₅)₄ was published by Trotter & Chieh (1970) and small differences were found between their lattice parameters and ours. A new calculation of the theoretical structure was carried out using their lattice parameters: $a=12.058$, $c=6.568$ Å. The values

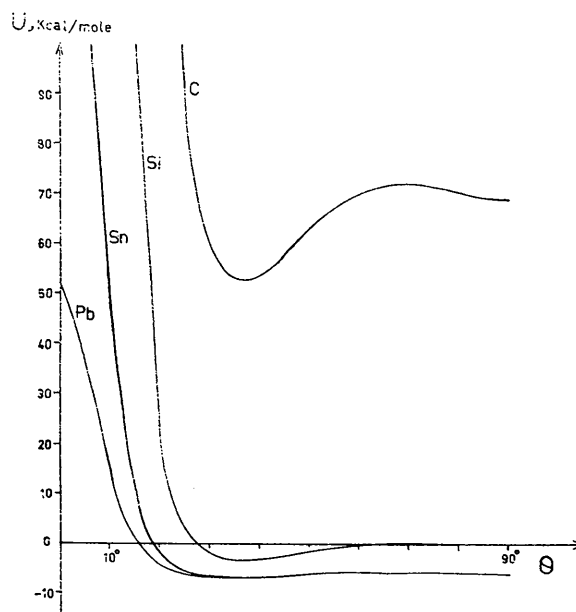


Fig. 1. Relation between U and θ for the four tetraphenyl compounds

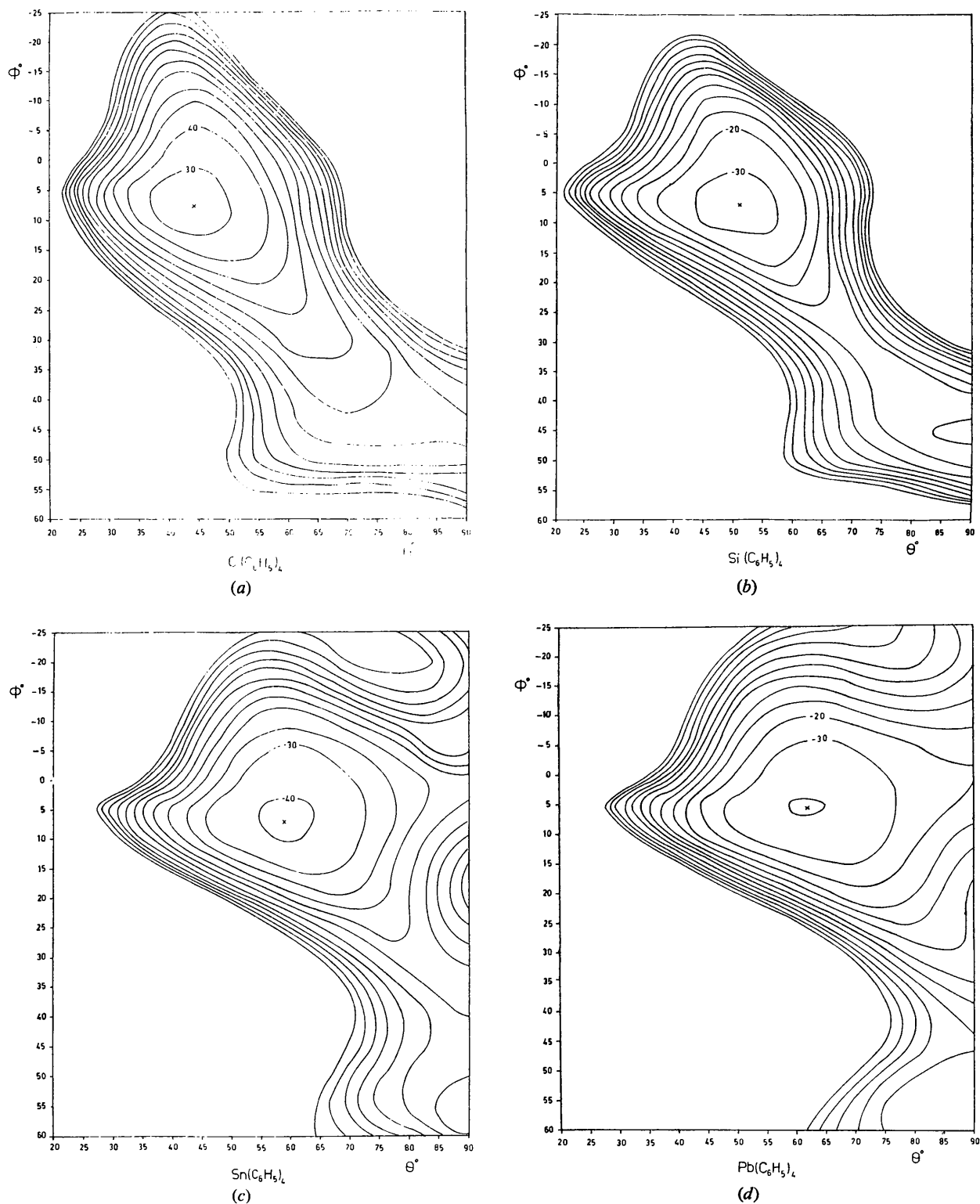


Fig.2. Variation of U_I with θ and ϕ .

Table 4. Comparison of experimental and theoretical coordinates

| Experimental coordinates of Ahmed & Alexandrov | | | Theoretical coordinates with $a=11.970$ and $c=6.604$ Å | | |
|---|--------|-------|--|--------|-------|
| x | y | z | x | y | z |
| 0.145 | -0.018 | 0.188 | 0.145 | -0.018 | 0.187 |
| 0.149 | -0.104 | 0.331 | 0.152 | -0.105 | 0.325 |
| 0.245 | -0.117 | 0.448 | 0.246 | -0.117 | 0.446 |
| 0.334 | -0.043 | 0.428 | 0.333 | -0.041 | 0.430 |
| 0.329 | 0.042 | 0.285 | 0.326 | 0.047 | 0.293 |
| 0.233 | 0.055 | 0.165 | 0.232 | 0.058 | 0.171 |

| Experimental coordinates of Chieh & Trotter | | | Theoretical coordinates with $a=12.058$ and $c=6.568$ Å | | |
|--|--------|-------|--|--------|-------|
| x | y | z | x | y | z |
| 0.145 | -0.019 | 0.185 | 0.144 | -0.018 | 0.188 |
| 0.151 | -0.107 | 0.331 | 0.152 | -0.107 | 0.322 |
| 0.247 | -0.117 | 0.447 | 0.246 | -0.118 | 0.444 |
| 0.339 | -0.041 | 0.427 | 0.331 | -0.041 | 0.432 |
| 0.329 | 0.045 | 0.294 | 0.323 | 0.048 | 0.299 |
| 0.233 | 0.058 | 0.165 | 0.229 | 0.059 | 0.177 |

Table 5. Lattice energies

| Compound | a | c | φ | U (kcal.mole ⁻¹) |
|---|----------|---------|-----------|-----------------------------------|
| C(C ₆ H ₅) ₄ | 10.735 Å | 7.278 Å | 7.5° | -32.633 |
| Si(C ₆ H ₅) ₄ | 11.326 | 6.889 | 7.5 | -34.30 |
| Sn(C ₆ H ₅) ₄ | 11.808 | 6.486 | 7.0 | -36.04 |
| Pb(C ₆ H ₅) ₄ | 12.033 | 6.380 | 5.5 | -35.88 |

of θ and φ obtained are 61° and 7°. These must be compared with the experimental values ($\theta=59$, $\varphi=7$) calculated using the new coordinates and parameters. Table 4 gives the experimental coordinates determined by Ahmed & Alexandrov (1970) and Trotter & Chieh (1970), and the theoretical values corresponding to their parameters.

Variation of lattice energies with lattice parameters

The lattice energies of the four compounds were calculated as a function of the lattice parameters and the angle of molecular orientation, φ . The values of the energy, the lattice parameters and angle φ corresponding to the minima are given in Table 5.

The difference between these lattice parameters, which must correspond to the structures at absolute zero, and those for room temperature (Table 1) obtained from X-ray measurements are within the permitted range. The values of the heats of sublimation of these compounds are not known so no comparison can be made with the values of the lattice energies.

All calculations were performed on the computers BESM-3M and BESM-6 using special programs.

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