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Lattice-Energy Calculations on Phenothiazine and Phenoselenazine Modifications

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Abstract

Lattice-energy calculations in the atom–atom potential approach have been performed for observed and isostructurally derived hypothetical forms of phenothiazine and phenoselenazine compounds. Energy minimizations with respect to cell constants and molecular rigid-body coordinates lead to absolute minima of energy surfaces in all cases. The experimental values of cell constants for the three

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observed structures are reproduced to better than 5% and the shifts of positional and orientational molecular parameters are lower than 0·1 Å and 2°, respectively.

Introduction

Packing analyses within the atom–atom approach have been carried out for a number of hydrocarbons with largely satisfying results but the method is also reasonably valid, as shown in the literature, for other organic molecules containing atoms other than C and H, especially when these atoms are partially screened by C and H.

In a previous work (Villares, Jiménez-Garay, Conde & Márquez, 1976) we successfully applied molecular-packing analysis for the determination of the then unknown crystal structure of phenoselenazine. We also modeled (Benavente, Conde & Márquez, 1975) the crystal packing of 3,7-dichlorophenoselenazine – the cell constants and molecular position and orientation, which had been found experimentally (Bernier, Conde & Márquez, 1974), were well reproduced after energy minimization.

In this paper we discuss the results of the van der Waals energy calculations performed for phenothiazine and phenoselenazine crystals. Molecules with a 'hollow' in the middle are not, as a consequence, very convenient for packing and several polymorphous modifications are encountered. For example, five acridine modifications (Phillips, 1954; Herbstein & Schmidt, 1955) and two polymorphous phenazines (Herbstein & Schmidt, 1955) have been reported. For phenothiazine a monoclinic (space group $P2_1$) form was studied (Bell, Blount, Briscoe & Freeman, 1968; Freeman, 1979) and then an orthorhombic (space group *Pnma*) modification was reported (McDowell, 1976). For phenoselenazine only an orthorhombic (space group $P2_12_12_1$) form is known (Villares, Jiménez-Garay, Conde & Márquez, 1976). In view of molecular similarities lattice-energy calculations were carried out for the observed and also for the isostructural derived forms of both compounds.

From the calculations it should be possible to establish whether or not hypothetical polymorphous varieties could be formed. Comparison between lattice energies calculated for the two compounds in the different space groups should also give information about the extent to which homologous molecules within a family of the Periodic Table can be expected to form isostructural crystals.

Description of the calculation

Lattice-energy calculations in the atom–atom potential approach were performed using the computer program *PCK*6 (Williams, 1972*b*). In this program the energy is taken as the sum of pairwise interactions between non-bonded atoms, using a Buckingham form $\varphi = -A/r^6 + B\exp[-Cr]$ for the potential functions describing interactions between pairs. Truncation errors in the van der Waals contributions are virtually eliminated by use of the Ewald–Bertaut–Williams technique for accelerated convergence (Bertaut, 1952; Williams, 1971). A limit of 6 Å was set to ensure convergence to 0·1 kJ mol^{-1} and some attempts with a larger sphere of interactions showed no influence on the location of energy minima. The program allows for minimization of the energy with respect to the structural parameters, that is, the cell constants and rigid-body positions and orientations.

Potential-function parameters assuming the atoms to be electrically neutral were used. Coefficients fitted by Williams (1972*a*) for the C and H atoms and by Govers (1975) for the N atom were selected. For the S···S interactions potential parameters were taken from Rinaldi & Pawley (1973), and for the Se···Se interactions parameters proposed by Govers (1979) were used. For mixed interactions the geometric-mean combining law was used for coefficients A and C, while B was fitted to give the minimum of the potential function at the sum of the respective van der Waals radii. All parameters used are listed in Table 1.

Lattice-energy calculations were made for all three ($P2_1$, $P2_12_12_1$ and *Pnma*) forms, either observed or hypothetical structures, of phenothiazine and phenoselenazine compounds. Intermolecular-energy minimizations were performed with respect to the cell constants and molecular rigid-body parameters. In $P2_1$, the position of the origin along the y axis being undetermined, there are nine independent variables to be minimized while in *Pnma*, because of the special positions of the molecules in the cell, only two translational and one rotational degree of freedom exist and, therefore, there are only six independent variables for this space group.

Table 1. *Non-bonded potential-function parameters*

The energy is in kJ mol^{-1} if r is in Å.

Interaction	A	B (×10^3)	C
H···H	101·95	9·07	3·74
C···H	467·41	35·54	3·67
C···C	2143·04	300·05	3·60
N···H	569·10	25·73	3·67
N···C	2609·20	217·29	3·60
N···N	3176·80	440·57	3·60
S···H	712·42	12·22	3·24
S···C	3266·32	86·22	3·17
S···N	3976·85	86·83	3·17
S···S	4978·38	42·22	2·80
Se···H	1083·93	50·59	3·54
Se···C	4969·60	434·38	3·47
Se···N	6050·64	415·07	3·47
Se···Se	11524·26	345·40	3·34

Of the six structures for which calculations were made, only three are known experimentally. For the known structures the initial cell constants and molecular position and orientation were those experimentally found; published coordinates for non-hydrogen atoms were used but H-atom positions were calculated for the expected geometry (Williams, 1965). For the hypothetical crystals, initial cell constants were the experimental values for the respective isostructural crystal and starting models were generated by using a grid for molecular translations and rotations according to the Cheshire group (Hirshfeld, 1968). The atomic coordinates of the trial model were calculated from values of bond lengths and angles, the dihedral angle value being that observed for experimental structures. There seems (Marsau, 1972) to be no packing influence to force the dihedral angle between the two halves of the molecule to differ from its intrinsic value, resulting from intramolecular interactions, so it seems that the degree of molecular folding in the crystals is close to that of the free molecules.

Results and discussion

Results of energy minimization for the observed structures are compared with the experimental data in Table 2. The molecular position and orientation are described by the centre-of-mass coordinates (x,y,z) and by Euler angles (θ,φ,ψ) which move (except for translation) the internal Cartesian coordinate system (inertia axes of the molecule) with respect to the fixed external Cartesian coordinate system based on the crystal axes. The difference between the experimental and calculated atomic coordinates is expressed as $\phi = (\sum_{i,N} \Delta_{i,N}^2/3N)^{1/2}$, where Δ_i is the difference in the ith Cartesian coordinate of each of the N atoms of the molecule (Zugenmaier & Sarko, 1972).

Experimental values of the cell constants for the three observed structures are reproduced to better than 5%. Only the c parameter in the *Pnma* form of phenothiazine shows a shift of 8%. In all cases calculated parameters are smaller than those observed. Since vibrational effects are ignored in the calculations reported herein, the unit cells measured at room temperature should contract during energy minimization. Agreement between the observed and calculated structure can be expressed by the shifts of the positional and orientational molecular parameters which are lower than 0·1 Å and 2°, respectively, in all cases. As a function of observed and calculated atomic coordinates, the agreement factor ϕ is in the range 1–2%. Another measurement of the agreement between the observed structure and the minimum of the potential-energy surface is based on an examination of the second derivatives of the energy evaluated at the point, on the energy surface, corresponding to the experimentally determined crystal structure. If the fit is good, all the eigenvalues of the matrix of the second derivatives will be positive (Williams, 1972*a*); that is, the experimental structure will be within the range of curvature of the calculated minimum. Such was the case for all the minimizations reported in this work.

For the hypothetical modifications, starting from the structural model described above, the energy was minimized by varying simultaneously the cell constants and the molecular degrees of freedom. The results are summarized in Table 3 in a way similar to that used for the observed forms. Lattice-energy maps show that the calculated structures correspond to real minima of the multidimensional energy surface.

Table 2. *Results of the energy minimization for observed structures*

	Phenothiazine				Phenoselenazine	
	$P2_1$		*Pnma*		$P2_12_12_1$	
	obs.	calc.	obs.	calc.	obs.	calc.
Cell						
a (Å)	7·82 (3)	7·57	7·916 (10)	7·77	7·829 (5)	7·62
b (Å)	5·93 (1)	5·59	20·974 (10)	20·39	20·909 (4)	20·55
c (Å)	10·70 (8)	10·58	5·894 (10)	5·43	5·927 (7)	5·93
β (°)	105·99*	106·6				
V (Å^3)	470·0	429·0	978·6	860·3	970·2	928·6
ϕ		0·017		0·015		0·006
K	0·67	0·73	0·64	0·73	0·68	0·71
Molecular coordinates						
x	−0·25	−0·29	2·33	2·19	2·23	2·14
y	1·82	1·84	5·24	5·10	3·14	3·09
z	3·11	3·09	0·04	0·08	2·29	2·30
θ (°)	97·0	98·4	146·5	146·5	142·5	143·6
φ (°)	146·7	145·6			93·8	92·3
ψ (°)	25·3	22·3			108·2	110·0
E (kJ mol^{-1})		−96·1		−94·8		−96·4

* In the paper of Bell *et al.* (1968) $\beta = 74·01°$ is given.

Table 3. *Results of the energy minimization for hypothetical structures*

	Phenothiazine	Phenoselenazine	
	$P2_12_12_1$	$P2_1$	*Pnma*
Cell			
a (Å)	7·30	7·87	8·59
b (Å)	20·91	6·07	19·65
c (Å)	5·69	10·33	5·85
β (°)		105·99	
V (Å^3)	868·5	474·4	987·4
K	0·72	0·69	0·66
Molecular coordinates			
x	2·50	−1·06	2·22
y	3·18	1·97	4·91
z	1·96	1·74	0·02
θ (°)	149·6	93·6	144·5
φ (°)	88·2	159·2	
ψ (°)	109·2	27·9	
E (kJ mol^{-1})	−93·3	−90·3	−81·2

In terms of the 'coefficient of molecular packing' (Kitaigorodsky, 1961): $K = ZV_o/V$, where V is the cell volume and Z the number of molecules of V_o volume in the cell, values obtained in all cases – observed and hypothetical forms – are in the range 0·6 to 0·8, characteristic of aromatics. If we consider calculated structures resulting from the minimization process, for phenothiazine the value of $K = 0{\cdot}73$ is the same for the two observed forms; this result agrees with the hypothesis of close packing (Kitaigorodsky, 1961) and indicates that the packing density has major effects on the energy of the crystal structure. On the other hand, the value $K = 0{\cdot}72$ for the hypothetical $P2_12_12_1$ structure shows no significant difference with respect to the value for the observed forms.

For phenoselenazine a value $K = 0{\cdot}71$ for the observed form is found, similar to the K value obtained for phenothiazine, as corresponds to similar molecules. In this case, smaller values of K are found for hypothetical forms ($K = 0{\cdot}69$ for $P2_1$ and $K = 0{\cdot}66$ for *Pnma*), in agreement with the rule that the densest mode of packing is that which actually occurs.

Within the limits of the approximate nature of the atom–atom approach and the validity of the potential functions used to describe the pair interactions, we think that the results obtained for density-packing coefficients and estimated lattice energies could indicate a higher probability of existence for the $P2_12_12_1$ form of phenothiazine and for the $P2_1$ form of phenoselenazine. In spite of the errors in E introduced by the summation limits which amount to several per cent (Williams, 1971), the energy calculated for the *Pnma* form of phenoselenazine is higher than that for the other forms. However, these calculations cannot imply, in our opinion, the non-existence of this form of phenoselenazine. On the other hand, the form *Pnma* is that experimentally found for dichlorophenoselenazine.

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