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Van der Waals Interactions and Molecular Packing in Crystals of Cubic α-Nitrogen, Orthorhombic Cyanogen and Monoclinic Octachlorocyclobutane

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The potential energy in molecular crystals of α-nitrogen, cyanogen and octachlorocyclobutane is calculated as a function of the unit-cell parameters. Some available potential functions for nitrogen–nitrogen and chlorine–chlorine interactions between non-bonded atoms are tested. The results show a good agreement between the unit-cell parameters obtained by the X-ray diffraction method and those corresponding to the deepest minimum of the potential energy, when suitable potential functions are used.

Introduction

It has previously been shown (Giglio & Liquori, 1967; Giglio, 1969) that when the molecular geometry of a molecular crystal and the crystal parameters and symmetries are known, the crystal packing may be predicted by locating the deepest minima of the intermolecular van der Waals and hydrogen bonding energies, which are computed as a function of all the rotational and translational degrees of freedom defining the coordinates of the asymmetric unit. This method was successfully applied to the determination of the molecular crystal structure of 5α-androstan-3,17-dione (Damiani, Giglio, Liquori & Mazzarella, 1967). Later, the relative validity of the potential functions used was tested in known crystal structures as a function of the unit-cell parameters, considering the molecules as rigid bodies and leaving the crystal symmetries unchanged. Some potential functions, relative to interactions involving hydrogen, carbon, oxygen and sulphur atoms, were verified for crystalline adamantane (Liquori, Giglio & Mazzarella, 1968), orthorhombic sulphur (Giglio, Liquori & Mazzarella, 1968) and polymeric sulphur trioxide (Giglio, Liquori & Mazzarella, 1969).

The results concerning nitrogen–nitrogen and chlorine–chlorine interactions reported here complete a set of potential functions which refer to the more common atoms in organic crystals.

Calculation of van der Waals Potential energy for α-nitrogen and orthorhombic cyanogen

It was decided to test some available nitrogen–nitrogen potential functions: the molecular crystals of α-nitrogen and cyanogen were chosen.

Table 1. *Potential function coefficients for nitrogen–nitrogen interactions*

The energy is in kcal per atom pair (if the interatomic distance is in Å).

Symbol of set	Reference	$A \cdot 10^{-3}$	B	C	D
a	1	387·0	0·000	354	12
b	2	161·0	0·000	363	12
c	3	243·0	0·000	547	12
*d**	4	1439·6	4·010	1557	0
e	5,6	30·1	3·779	232	0
f	5,6	30·1	4·193	124	0

(1) Parsonage & Pemberton, 1967.
(2) Scott & Scheraga, 1966.
(3) Brant, Miller & Flory, 1967.
(4) Mason & Rice, 1954.
(5) Kitaigorodsky, 1961.
(6) Venkatachalam & Ramachandran, 1967.

* Mason and Rice proposed two functions. The first, reported here, fits the crystal properties well and the second Virial coefficients of nitrogen; the second one, which fits the viscosity coefficients, gives very slightly different results.

Solid α-nitrogen is cubic, space group $Pa3$, with a lattice parameter of 5·66 Å (Vegard, 1929; Ruhemann, 1932; Bolz, Boyd, Mauer & Peiser, 1959; Hörl & Marton, 1961). A model of the face centred cubic cell is shown in Fig. 1.

The potential energy changes with respect to the unit-cell edge **a** were calculated by use of the set of parameters, corresponding to the various potential functions tested, reported in Table 1 in the generalized form

$$V(\mathbf{r}) = \frac{A\exp(-Br)}{r^D} - \frac{C}{r^6}$$

(de Coen, Elefante, Liquori & Damiani, 1967). A value

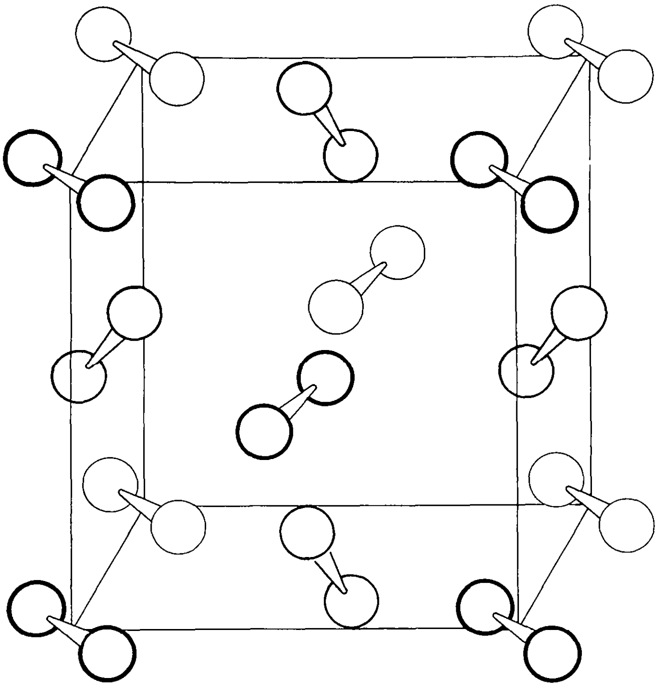

Fig. 1. Cubic cell of α-nitrogen.

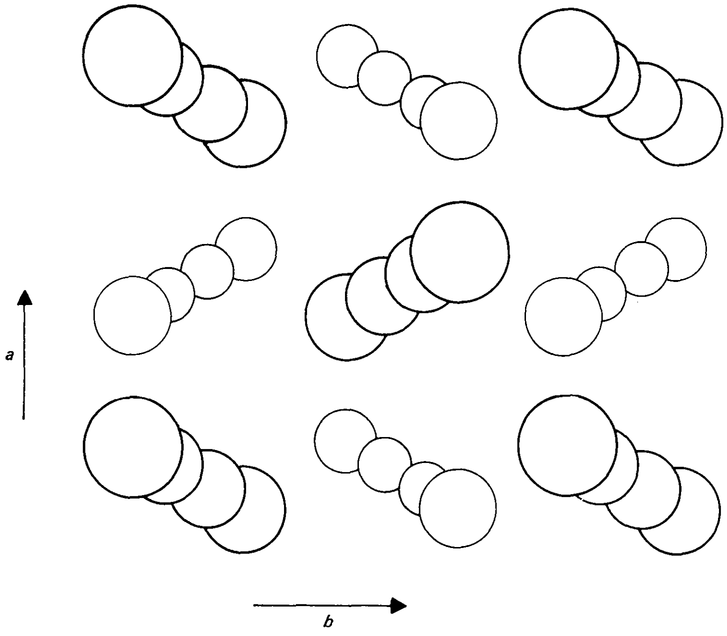

Fig. 2. Projection of the structure of solid cyanogen along its c axis.

of 1·098 Å was taken for the intramolecular distance N–N, as given by Stoicheff (1954).

The calculations were performed by taking into account the interactions between one nitrogen atom and the twelve molecules nearest to it. The unit-cell volume was adjusted by varying the parameter a in the range 3·50–7·00 Å in increments of 0·05 Å.

The results are summarized in Table 2 where

$$\Delta a/a=(a_{\text{calc}}-a_{\text{obs}})/a_{\text{obs}}\ .$$

The same potential functions were also verified, together with carbon–carbon and carbon–nitrogen potential functions, for the crystal structure of orthorhombic cyanogen.

Table 2. *Values of the parameter a and percentage errors corresponding to the deepest minima found in the analysis of α-nitrogen*

Symbol of set	a	$\Delta a/a$
a	5·55 Å	−1·8%
b	4·85	−14·2
c	4·85	−14·2
d	6·15	8·8
e	5·35	−5·3
f	4·90	−13·3

Solid cyanogen crystallizes in the space group *Pcab*, $Z=4$. The unit-cell parameters are:

$$a=6{\cdot}31\ ;\ b=7{\cdot}08\ ;\ c=6{\cdot}19\ \text{Å}\ .$$

The intramolecular distances C–C and C–N were taken to be 1·37 and 1·13 Å respectively as determined by X-ray diffraction (Parkes & Hughes, 1963). The molecule is linear to within half a degree; the molecular packing is shown in Fig. 2. A three-dimensional energy map was computed from the potential functions of Table 3 taking into account all the van der Waals interactions between the atoms of one C_2N_2 molecule and those of the eighteen molecules nearest to it. Translational increments of 0·1 Å were used and the unit-cell parameters were varied within the ranges:

$$4{\cdot}5\le a\le 7{\cdot}3\ \text{Å}$$
$$5{\cdot}5\le b\le 8{\cdot}0$$
$$5{\cdot}2\le c\le 7{\cdot}8\ .$$

Table 4 summarizes the results of the analysis.

Table 3. *Potential function coefficients for carbon–carbon, carbon–nitrogen and nitrogen–nitrogen interactions*

The energy is in kcal per atom pair (if the interatomic distance is in Å).

	C–C					C–N					N–N				
Symbol of set	Reference	$A\,.\,10^{-3}$	B	C	D	Reference	$A\,.\,10^{-3}$	B	C	D	Reference	$A\,.\,10^{-3}$	B	C	D
g	1	301·0	0·000	327	12	*	340·0	0·000	340	12	2	387·0	0·000	354	12
h	3	286·0	0·000	370	12	3	216·0	0·000	366	12	3	161·0	0·000	363	12
i	4	396·0	0·000	364	12	4	337·0	0·000	572	12	4	243·0	0·000	547	12
l	1	301·0	0·000	327	12	*	600·2	2·005	714	6	5	1439·6	4·010	1557	0
m	6,7	30·1	3·439	408	0	6,7	30·1	3·601	310	0	6,7	30·1	3·779	232	0
n	6,7	30·1	3·824	216	0	6,7	30·1	4·193	124	0	6,7	30·1	4·000	165	0
o	2	408·0	0·000	373	12	2	483·0	0·000	363	0	2	387·0	0·000	354	12

(1) Bartell, 1960.
(2) Parsonage & Pemberton, 1967.
(3) Scott & Scheraga, 1966.
(4) Brant, Miller & Flory, 1967.
(5) Mason & Rice, 1954.
(6) Kitaigorodsky, 1961.
(7) Venkatachalam & Ramachandran, 1967.

* The attractive coefficient and the exponential factor of the mixed interaction were obtained by averaging geometrically respective terms of the C–C and N–N functions. The repulsive parameter was then calculated by minimizing the complete function at a distance corresponding to the sum of the carbon and nitrogen van der Waals radii.

Calculation of van der Waals potential energy for octachlorocyclobutane

Although the structure of crystalline chlorine is known (Collin, 1952, 1956), the study of another compound to test chlorine–chlorine interactions was preferred because this halogen crystallizes in the unexpected *Cmca* space group (Nyburg, 1964; Hillier & Rice, 1967; Townes & Dailey, 1952) and presents some short contacts. The crystal structure of octachlorocyclobutane appeared to be interesting because the carbon atoms are screened by the outermost chlorine atoms which control the molecular packing. Octachlorocyclobutane crystallizes (Owen & Hoard, 1951) in a two-molecule monoclinic unit cell, space group $P2_1/m$, with a = 8·00, b = 10·64, c = 6·28 Å; β = 107°45′. The atomic coordinates refined by the least-squares method (Margulis, 1965) were used in the present analysis. The crystal packing is shown schematically in Fig. 3.

The potential energy was calculated as a function of β, a, b and c, using the potential functions of Table 5 and considering all the van der Waals interactions between the atoms of one C_4Cl_8 molecule and those of the twelve molecules nearest to it. Angular and translational increments of 10° and 0·3 Å were given in the first run. The parameters varied in the ranges:

$$90° \leq \beta \leq 180°$$
$$7{\cdot}3 \leq a \leq 8{\cdot}6 \text{ Å}$$
$$8{\cdot}8 \leq b \leq 10{\cdot}8$$
$$5{\cdot}6 \leq c \leq 6{\cdot}9\,.$$

The regions of the minima were explored by means of a second run with increments of 1° and 0·1 Å. Table 6 shows the results thus obtained.

Discussion

From inspection of Tables 2, 4 and 6 it follows clearly that the N–N and Cl–Cl interactions may be described well by means of the parameters proposed by Parsonage & Pemberton (1967) and by Mason & Rice (1954) respectively and that the reliability of the carbon–carbon potential function of Bartell (1960) is again confirmed. However, the carbon–carbon, carbon–nitrogen and carbon–chlorine interactions play a minor role in determining the minimum of energy, because the distances which refer to these atoms are generally greater than the nitrogen–nitrogen and chlorine–chlorine distances. Numerical calculations show that the energy gradients, due only to the nitrogen–nitrogen or chlorine–chlorine interactions, are the steepest for the

Table 4. *Values of the parameters a, b and c and percentage errors corresponding to the deepest minima found in the analysis of cyanogen*

Symbol of set	a	$\Delta a/a$	b	$\Delta b/b$	c	$\Delta c/c$
g	6·3 Å	0·0%	7·3%	2·8%	6·1 Å	−1·6%
h	5·3	−15·9	6·4	−9·9	6·7	8·1
i	5·3	−15·9	6·4	−9·9	6·8	9·7
l	6·9	9·5	7·8	9·9	6·4	3·2
m	5·8	−7·9	6·8	−4·2	7·2	16·1
n	5·3	−15·9	6·3	−11·3	6·7	8·1
o	6·0	−4·8	7·0	−1·4	7·3	17·8

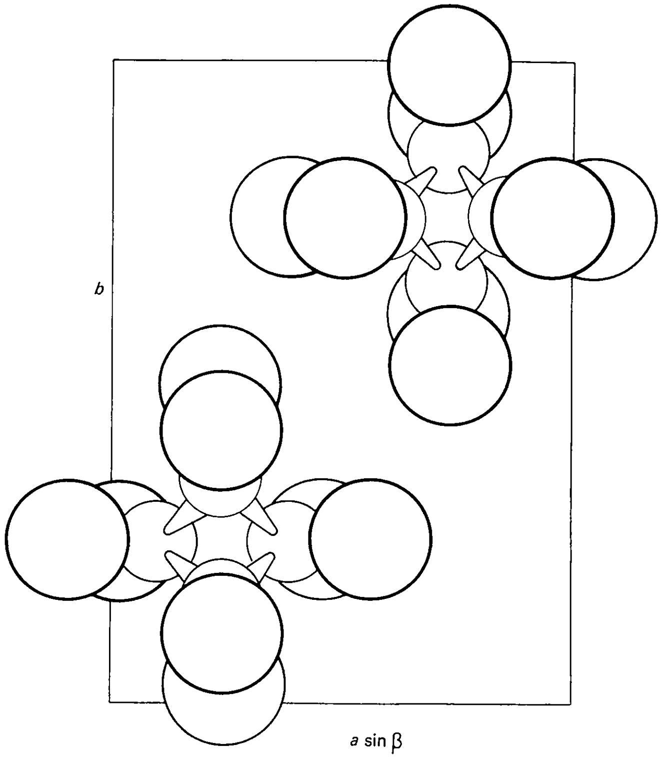

Fig. 3. Molecular packing of octachlorocyclobutane.

Table 5. *Potential function coefficients for carbon–carbon, carbon–chlorine and chlorine–chlorine interactions*

The energy is in kcal per atom pair (if the interatomic distance is in Å).

	C–C					C–Cl					Cl–Cl				
Symbol of set	Reference	*A* . 10⁻³	*B*	*C*	*D*	Reference	*A* . 10⁻³	*B*	*C*	*D*	Reference	*A* . 10⁻³	*B*	*C*	*D*
p	1	301·0	0·000	327	12	*	239·0	3·970	653	0	2	220·8	3·620	1430	0
q	1	301·0	0·000	327	12	*	248·0	4·000	732	0	3	259·7	3·670	1811	0
r	4	528·0	4·580	370	0	4	425·0	4·170	975	0	4	314·0	3·750	2520	0
s	5	37·7	3·510	474	0	5	64·7	3·510	818	0	5	229·0	3·510	2900	0

(1) Bartell, 1960.
(2) Mason & Rice, 1954.
(3) Hill, 1948.
(4) Scott & Scheraga, 1965.
(5) Kitaigorodsky & Dashevsky, 1968.

* See footnote to Table 3.

Table 6. *Values of the parameters β, a, b and c and percentage errors corresponding to the deepest minima found in the analysis of octachlorocyclobutane*

Symbol of set	β	$\Delta\beta$	a	$\Delta a/a$	b	$\Delta b/b$	c	$\Delta c/c$
p	105°	−3°	8·0 Å	0·0%	10·2 Å	−3·8%	6·3 Å	0·0%
q	105	−3	7·9	−1·3	10·0	−5·7	6·2	−1·6
r	105	−3	7·7	−3·7	9·6	−9·4	6·0	−5·0
s	105	−3	7·9	−1·3	9·9	−6·6	6·2	−1·6

cases of cyanogen and octachlorocyclobutane respectively. The best results are given by the sets *a*, *g* and *p*. All sets give the same good agreement with respect to the angle *β* in the crystal of octachlorocyclobutane, as in the case of polymeric sulphur trioxide, since the angular displacements influence the intermolecular approaches much more.

It is interesting to observe that the potential functions of set *p* are the same as those which allowed us to calculate satisfactorily pairwise interactions between two carbon tetrachloride molecules in the gas phase, the potential barrier hindering rotation in hexachloroethane (de Coen, Elefante, Liquori & Damiani, 1967) and the conformational potential energy of polypeptides (Liquori, 1969).

The calculations reported above show therefore that potential functions are available which allow us to calculate unit-cell parameters of the crystals studied with an accuracy which is satisfactory for the purpose of using such functions to predict crystal structures or conformations of macromolecules by energy minimization procedures.

Finally it must be stressed that, generally, the minima correspond to decreases of volume as in previous cases (Liquori, Giglio & Mazzarella, 1968; Giglio, Liquori & Mazzarella, 1968; Giglio, Liquori & Mazzarella, 1969), and that temperature effects and lattice vibrations were not taken into account.

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Operation of a Computer-Controlled Equi-Inclination X-ray Diffractometer

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The control program for a Buerger–Supper equi-inclination diffractometer on-line to a PDP–8/S computer is described. The computer calculates the angular settings, scan-range and optimum scan-speed for each reflexion, pulses stepping motors to provide the crystal and counter motions, inserts attenuators or balanced filters, and activates and interrogates the scaler which is part of the standard counting circuitry. A careful choice of counter apertures, and the re-measurement of reflexions whose precision or background imbalance fails to meet pre-set criteria, appear to overcome the major systematic errors to which diffractometer data recorded in the equi-inclination ω-scan mode are subject.

The Buerger single-crystal equi-inclination diffractometer (Buerger, 1960*a*) has been commercially available for some years in the form of the Supper–Pace Automatic Diffractometer,§ incorporating standard counting circuits and a small fixed-logic computer. The replacement of this fixed-logic computer by a PDP–8/S digital computer with appropriate low-level interfaces|| produces a relatively low-cost installation of surprising versatility (Fig. 1).¶

Instrumentation

The variables μ and ν (equi-inclination angles), Υ (counter setting) and φ (crystal setting) for this type of diffractometer have been defined by Buerger (1960*b*,*c*). The values of μ and ν are adjusted manually for each reciprocal-lattice layer. Within a layer, the counter and crystal are moved to their respective settings, Υ and φ, for each reflexion by two Digitork stepping motors** operating under computer control.

The counting chain consists of standard Philips electronic components (scintillation counter, pulse-height analyser, scaler, rate-meter, printer- and punch-control units). Counts are initiated by impulses from the computer to the scaler and are timed by an electronic clock in the computer.

Some physical constants of the equipment are as follows: X-ray source-to-crystal distance, 14·5 cm; crystal-to-counter distance, 7·5 cm; $0 \leq \mu, \nu \leq 55°$; the lower limit of Υ is $-10°$ and the upper limit is given empirically by $\Upsilon \leq 73 + 65[1-(\mu/55)^2]^{1/2}$. The motors are geared to give a resolution of 0·01 degree per step on the Υ and φ scales. The maximum slewing speed of both motors, operating singly or simultaneously under computer control, is 3 deg.sec^{-1}. The PDP–8/S computer has a memory of 4K twelve-bit words, a cycle time of 8 μsec and an addition-time of 36 μsec.

Input to the system is from the keyboard or tape-reader of an ASR–33 Teletype unit, and output is *via* the same unit both in printed and punched-tape form. There are provisions for the programmed insertion of balanced filters, attenuators or a fast-acting shutter, for the manual operation of one or both motors, and for the mechanical interruption of power to the Υ-motor in the event of the counter colliding with any part of the equipment.

The control program

The program (which was written almost entirely by J. M. G. and C. E. N.) consists of a number of routines which perform the following functions: Input (cell parameters, constants for scan-range calculation and control parameters); calculation and listing of crystal and counter settings for a single reflexion or for a

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|| Digital Equipment Corp., 146 Main Street, Maynard, Mass. 01754, U.S.A.

¶ A detailed User Manual and an expanded version of this paper are available.

** Model No. M218TW, Motion Control Systems Division, Warner Electric Brake & Clutch Co., Beloit, Wis. 53511, U.S.A.