

tion d'une structure nécessite, dans le cas de molécules dont la rigidité peut être mise en doute, quelques précautions. L'examen de la molécule 7 montre clairement que des résultats qui semblent relativement corrects peuvent être sensiblement modifiés dans une analyse qui introduit une hypothèse supplémentaire (ici la possibilité d'oscillation indépendante des cycles). Les tests de Burns, Ferrier & McMullan, bien qu'assez subjectifs, comme le font remarquer leurs auteurs, sont d'une grande utilité pour la discussion des différentes analyses. Enfin, dans le cas où les deux blocs ont des masses très différentes, l'hypothèse de l'oscillation indépendante des cycles se révèle nécessaire à la description du mouvement de la molécule.

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Van der Waals and Electrostatic Interactions in Crystals

BY G. CAPACCIO, P. GIACOMELLO AND E. GIGLIO

Laboratorio di Chimica Fisica, Istituto Chimico, Università di Roma, Italy

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Some potentials describing electrostatic interactions between oxygen and sodium, potassium, rubidium and caesium ions are tested in known organic crystal structures. The atomic and ionic coordinates may be predicted satisfactorily by locating the deepest minimum of the potential energy which depends on rotational and translational degrees of freedom.

As part of a research programme developed to study the conformational stability of synthetic polymers and biopolymers and to solve the phase problem in crystals when the molecular geometry is approximately known, an analysis of some potentials accounting for the van der Waals interactions between non-bonded atom pairs, and the formation of hydrogen bonds, has previously been carried out (Liquori, 1969; Di Nola & Giglio, 1970; Giglio, 1969; Giacomello & Giglio, 1970 and references cited therein).

In the present paper we attempt to elucidate the role of the electrostatic interactions in simple crystals in order to evaluate the use of semi-empirical potential functions suitable for determining the positions of atoms and ions in organic crystals. We describe the investigation of crystalline compounds in which electrostatic interactions between oxygen, on the one hand, and sodium, potassium, rubidium and caesium ions, on the other, are present.

The semi-empirical potentials

Three kinds of potential, referred to as atom-atom, atom-ion and ion-ion, have been considered.

The coefficients of the atom-atom potential

$$V(r) = \frac{a \exp(-br)}{r^{\bar{a}}} - \frac{c}{r^6}$$

describing pairwise interactions between hydrogen, carbon and oxygen non-bonded atoms have been reported previously (Giglio, 1969).

Some noble gas potentials have been successfully employed for the alkali metal ions as well as for sulphur (Giglio, Liquori & Mazzarella, 1968), chlorine (Di Nola & Giglio, 1970), bromine and iodine atoms (Giglio, 1970) allowing us to account for the van der Waals atom-ion and ion-ion interactions. This latter case refers to Na^+-Na^+ , K^+-K^+ , Rb^+-Rb^+ and Cs^+-Cs^+ van der Waals interactions to which the usual coulombic term, with charges equal to unity, has been added. The energy calculations were performed with potential functions proposed by Mason & Rice (1954) and Kane (1939) for Ne, Ar, Kr, Xe and by Miller (1960) and Chakraborti (1966) for Rn. Their coefficients are given in Table 1.

The potentials corresponding to the two rare gases preceding and following the alkali metal in the periodic

Table 1. *The coefficients of the van der Waals Na⁺-Na⁺, K⁺-K⁺, Rb⁺-Rb⁺ and Cs⁺-Cs⁺ potential functions*

The energy is in kcal/atom pair if the interatomic distance is in Å.

Interaction	$a(\times 10^{-3})$	b	c	d
Ne-Ne ^a	105.7	4.608	125.1	0
Ne-Ne ^b	147.5	4.782	116.1	0
Ar-Ar ^a	220.8	3.621	1,430.0	0
Ar-Ar ^b	11,954.5	4.782	1,258.4	0
Kr-Kr ^a	65.8	3.033	2,733.8	0
Kr-Kr ^b	31,353.4	4.782	2,132.9	0
Xe-Xe ^a	174.2	2.921	6,626.0	0
Xe-Xe ^b	264,991.4	4.782	5,096.0	0
Rn-Rn ^c	102,656.0	0.000	15,383.2	12
Rn-Rn ^d	58,082.3	0.000	11,369.9	12

(a) Mason & Rice (1954)

(b) Kane (1939)

(c) Miller (1960)

(d) Chakraborti (1966)

table of the elements have been tested for each ion. These functions have been used to compute the parameters of the mixed atom-ion interactions as reported in Table 2.

Table 2. *The coefficients of the mixed potential functions have been calculated as reported by Di Nola & Giglio (1970), using Bartell's (1960) potentials for hydrogen and carbon atoms*

The energy is in kcal/atom pair if the interatomic distance is in Å.

Interaction	$a(\times 10^{-3})$	b	c	d
H-Ne=H-Na ^{+a}	26.2	4.344	78.5	0
H-Ne=H-Na ^{+b}	31.1	4.431	75.6	0
H-Ar=H-Na ⁺ , H-K ^{+a}	40.5	3.851	265.2	0
H-Ar=H-Na ⁺ , H-K ^{+b}	233.8	4.431	248.8	0
H-Kr=H-K ^{+a}	25.7	3.557	366.7	0
H-Kr=H-K ^{+b}	359.9	4.431	323.9	0
C-Ne=C-Na ^{+a}	188.6	2.304	202.3	6
C-Ne=C-Na ^{+b}	227.0	2.391	194.9	6
C-Ar=C-Na ⁺ , C-K ^{+a}	255.4	1.811	684.0	6
C-Ar=C-Na ⁺ , C-K ^{+b}	1,677.6	2.391	641.7	6
C-Kr=C-K ⁺ , C-Rb ^{+a}	149.0	1.517	945.0	6
C-Kr=C-K ⁺ , C-Rb ^{+b}	2,559.7	2.391	835.4	6
C-Xe=C-Rb ⁺ , C-Cs ^{+a}	249.6	1.461	1,472.4	6
C-Xe=C-Rb ⁺ , C-Cs ^{+b}	6,254.8	2.391	1,291.3	6
C-Rn=C-Cs ^{+c}	6,026.6	0.000	2,243.5	12
C-Rn=C-Cs ^{+d}	4,442.0	0.000	1,928.8	12

(a) Mason & Rice (1954)

(b) Kane (1939)

(c) Miller (1960)

(d) Chakraborti (1966)

The following ion-ion potential function

$$V(r) = \frac{Z^+Z^-}{r} + a \exp(-br)$$

containing an electrostatic term and the Born-Mayer repulsive potential was verified for the ionic oxygen-

alkali metal interactions. Here r is the interionic distance and Z^+ and Z^- the effective ionic charges, taken as unity except for the oxygen of the oxalate and formate ions ($Z^- = -0.5$). The van der Waals attractive term was neglected since it does not appreciably affect the results when included in the calculations. The b parameter has been evaluated from the room temperature approximation of the Born-Haber cycle for the oxides of alkali metals (Baughan, 1959), assuming the value of -142 kcal/g atom for the two-stage electron affinity of oxygen. The weighted mean value $b = 2.85$ Å⁻¹ was adopted for all the ion-ion potentials.

The repulsive coefficient a was estimated by minimizing the complete function at a distance r_m chosen on the basis of a set of empirical atomic radii, proposed by Bragg (1920) and Slater (1965), reproducing the observed interatomic distances in several hundred crystals. These radii agree well with those of maximum radial charge density in the outermost shells of the corresponding atoms, as derived by relativistic self-consistent field calculation including exchange correction (Lieberman, Waber & Cromer, 1965).

The ion-ion energy curves employed in this paper are shown in Fig. 1 and their characteristic parameters listed in Table 3.

Table 3. *Parameters of the mixed ion-ion potentials*

The energy is in kcal/ion-pair if the distance is in Å.

Interaction	Z^+Z^- (kcal × Å)	a (kcal/ion-pair)	r_m (Å)
Na-O	-165.75	11,559.41	2.50
K-O	-331.50	35,124.94	2.70
Rb-O	-331.50	60,034.65	2.95
Cs-O	-331.50	103,776.08	3.20

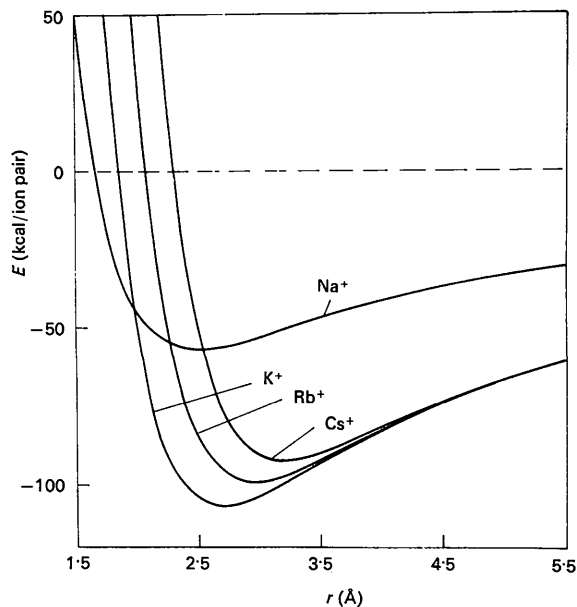


Fig. 1. Energy curves of the alkali-oxygen ion interactions. The ionic charge is ± 1 except in the case of the Na⁺ curve where it is -0.5 on the oxygen atom.

Table 4. Atomic fractional coordinates of the oxalate ion asymmetric unit which refer to the van der Waals energy minimum $\psi_1=72$, $\psi_2=154$ and $\psi_3=52^\circ$ (first three columns) compared with the experimental ones (last three columns)

The distances between corresponding atoms are given in the fourth column.

	X/a	Y/b	Z/c	$d(\text{\AA})$	X/a	Y/b	Z/c
C(1)	0.064	0.041	0.103	0.01	0.064	0.040	0.107
O(1)	0.154	-0.113	0.149	0.05	0.152	-0.114	0.163
O(2)	0.068	0.266	0.210	0.07	0.067	0.260	0.228

Sodium oxalate and formate

The first potential of Table 3 was checked for the known crystal structure of sodium oxalate (Jeffrey & Parry, 1954), which belongs to the space group $P2_1/a$, with $a=10.35$, $b=5.26$, $c=3.46$ Å; $\beta=92^\circ 54'$; $Z=2$. The centres of symmetry of the oxalate ions, possessing three Eulerian rotational degrees of freedom ψ_1 , ψ_2 and ψ_3 (Giglio & Liquori, 1967), are at $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, 0)$. The sodium ions may be translated along three directions so that the number of degrees of freedom is six. To save computing time we first found the van der Waals energy minimum of the oxalate group and then pursued the analysis by inserting the sodium ions in the crystal unit cell. The model of the oxalate ion, is nearly identical with the experimental one (Jeffrey & Parry, 1954), the bond lengths being equal to within 0.01 Å and the bond angles to within 0.7°. Fig. 2 shows the starting position of the model.

The minimum of the van der Waals energy of the oxalate ions was located at $\psi_1=72$, $\psi_2=154$ and $\psi_3=52^\circ$ by using angular increments of 4° and by considering all the intermolecular interactions between one molecule and the twenty nearest neighbours. The corresponding atomic coordinates agree well with those of Jeffrey & Parry (1954) as shown in Table 4.

The sodium ions were taken into account in the second stage of the minimum energy search, and intramolecular and intermolecular van der Waals and electrostatic interactions evaluated for a set of molecules consisting of a central one and the twenty-two closest neighbours. Moving from the minimum previously determined and keeping the oxalate ions fixed, the Na⁺s were allowed to translate along three orthogonal directions X , Y and Z until they reached an energy minimum. The strategy of this minimization technique is as follows. An increment of ± 0.06 Å by which the variable X may change is added to the original point to find the direction in which lower energy lies. If a successful change occurs, the X coordinate assumes its new value (otherwise it is left unchanged) and the same procedure is then repeated for Y and Z . This analysis is renewed until it fails to decrease the energy. Thereafter the increment is halved and the same process applied anew. Then the minimum search is continued by varying the three rotational degrees of freedom of the oxalate ion in the range $\pm 4^\circ$ with increments of 2°. Starting again from the point at deeper energy the entire cycle is car-

ried out repeatedly until the energy improvement is less than a prespecified amount, 0.001 kcal.

It is noteworthy that the Na⁺s always reach the same position even though their starting coordinates differ by more than 1 Å from the final ones. The results obtained by using the inert gas potentials of Ne and Ar for Na⁺ are summarized in the first four rows of Table 5.

Table 5. Distances between the atomic and ionic positions found in this analysis and the experimental ones for sodium oxalate and formate

Ka and MR indicate that the calculations have been performed by using the rare gas functions proposed by Kane (1939) and Mason & Rice (1954) respectively.

	Ne(Ka)	Ne(MR)	Ar(Ka)	Ar(MR)
Na	0.29 Å	0.29 Å	0.20 Å	0.20 Å
C(1)	0.07	0.07	0.05	0.05
O(1)	0.18	0.18	0.12	0.12
O(2)	0.28	0.28	0.26	0.26
Na	0.23	0.23	0.19	0.19
H	0.16	0.16	0.12	0.12
C(1)	0.16	0.16	0.12	0.12
O(1)	0.17	0.17	0.13	0.13
O(2)	0.17	0.17	0.13	0.13

Sodium formate (Zachariasen, 1940) is monoclinic, space group $C2/c$, with:

$$a=6.19, b=6.72, c=6.49 \text{ \AA}; \beta=121^\circ 42'; Z=4.$$

The carbon and hydrogen atoms and the sodium ions are in special positions 4(e) (*International Tables for X-ray Crystallography*, 1965) and the oxygen atoms in general positions 8(f). The sodium ion has one translational degree of freedom along the b axis as has the formate ion, which possesses one further rotational degree of freedom around the C-H bond assumed to be parallel to b and 1.08 Å long.

The potentials of sodium oxalate and in addition those involving the hydrogen atoms were used (see Table 2). All the intramolecular and intermolecular interactions in a group of nineteen molecules were estimated. Angular and translational increments of 2° and 0.04 Å were adopted in the minimum search. The results are reported in the last five rows of Table 5,

Potassium methoxide and potassium, rubidium and caesium acetylenediolate

Potassium methoxide (Weiss, 1963) is tetragonal, space group $P4/nmm$, with:

$$a = 3.94_9, c = 8.76_8 \text{ \AA}.$$

All the atoms except the hydrogen are in special positions $2(c)$ (*International Tables for X-ray Crystallography*, 1965). The C-H bonds were all assumed to be 1.08 Å long and all the bond angles at the carbon atom to be $109^\circ 28'$. There are two translational degrees of freedom along the c axis of the potassium and methylate ions and one rotational of the methyl hydrogens around the C-O bond parallel to c .

The appropriate potential functions of Table 1 and 2 together with the second one of Table 3 describe all the interactions involved in a block of nineteen molecules. Angular and translational increments of 10° and 0.02 \AA were used to find the energy minimum. The agreement between the calculated and experimental results is shown in the first three rows of Table 6. The hydrogen atoms are not reported since their coordinates were not established by X-ray analysis.

Potassium (Weiss & Büchner, 1963), rubidium and caesium (Weiss & Büchner, 1964) acetylenediolates are isostructural. The crystals are tetragonal, space group $I4/mmm$, with:

$$\begin{array}{lll} \text{K}_2\text{O}_2\text{C}_2 & a = 3.92_7, & c = 12.75 \text{ \AA}; & Z = 2 \\ \text{Rb}_2\text{O}_2\text{C}_2 & a = 4.13_3, & c = 13.04_9 \text{ \AA}; & Z = 2 \\ \text{Cs}_2\text{O}_2\text{C}_2 & a = 4.37_1, & c = 13.52_3 \text{ \AA}; & Z = 2. \end{array}$$

The atoms are in special positions $4(e)$. Since the geometry of the anion is known there is only one translational degree of freedom of the cations along the c axis.

The appropriate potentials of Table 1, 2 and 3 were used in computing the energy for a block of nineteen molecules. A translational increment of 0.02 \AA was employed in the minimum search and the last three rows of Table 6 show the results obtained for the three compounds.

Concluding remarks

The satisfactory results reported in Tables 5 and 6 lead us to place some confidence in the reliability of the potentials adopted for the solution of the phase prob-

lem in crystals. However it must be stressed that quantitative estimates of the energies are meaningless.

One difficulty which precludes a quantitative treatment is the discrepancy among the values of the effective ionic charges derived by a wide variety of methods (Levin, Syrkin & Dyatkina, 1969). Calculations were carried out for sodium oxalate and formate with the ionic charges varying over a rather large range, $0.5 \leq Z^+ \leq 1$ and $-0.5 \leq Z^- \leq -0.25$, but preserving the electroneutrality of the systems. All the values of the electrostatic energy are multiplied by a constant factor when the ionic charges are changed. The positions of the minima are only very slightly altered as the charges vary, since the coulombic term plays a dominant role in their determination.

Another problem is the evaluation of the dielectric constant which is a function of the translational and rotational degrees of freedom for every electrostatic interaction. As a reasonable approximation we have taken into account only the interactions between one molecule and the first shell of molecules surrounding it, putting the dielectric constant as unity. The inclusion of further shells in the calculations gives rise to unsatisfactory results.

The interionic separation r_m in the ion-ion potentials is a critical parameter in the minimum search. As an ex-

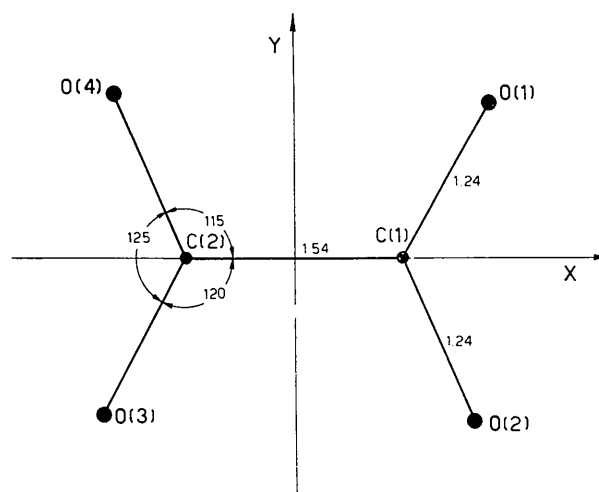


Fig. 2. Atomic numbering and position of the oxalate ion, lying in the XY plane, corresponding to $\psi_1 = \psi_2 = \psi_3 = 0^\circ$. Bond lengths and bond angles are shown.

Table 6. Distances between calculated and observed atomic and ionic positions for potassium methoxide and potassium, rubidium and caesium acetylenediolates

Ka, MR, M and Ch indicate that the calculations have been carried out by means of noble gas potentials proposed by Kane (1939), Mason & Rice (1954), Miller (1960) and Chakraborti (1966) respectively.

	Ar(Ka)	Ar(MR)	Kr(Ka)	Kr(MR)	Xe(Ka)	Xe(MR)	Rn(M)	Rn(Ch)
K	0.16 Å	0.20 Å	0.14 Å	0.20 Å				
C	0.20	0.18	0.24	0.20				
O	0.20	0.18	0.24	0.20				
K	0.07	0.10	0.02	0.08				
Rb			0.09	0.15	0.03 Å	0.06 Å		
Cs					0.01	0.09	0.02 Å	0.02 Å

ample good atomic coordinates were only achieved by using r_m values in the range 2.50 to 2.60 Å and 2.40 to 2.60 Å for sodium oxalate and formate respectively. The best agreement for both salts corresponds to $r_m = 2.60$ Å and in this case an appreciable improvement is obtained with respect to the results given in Table 5 ($r_m = 2.50$ Å). Because of our limited experience we cannot exclude the possibility that further analyses will lead to a modification of the r_m values of Table 3.

From Tables 5 and 6 it is clear that the best potentials for van der Waals atom-ion and ion-ion interactions are in general those of the rare gases following the alkali metals. It is perhaps significant that the van der Waals radii of the 'best' noble gases are about 1.90, 2.00, 2.20 and 2.40 Å for Ar, Kr, Xe and Rn, corresponding to Slater's ionic radii 1.80, 2.20, 2.35 and 2.60 Å for Na, K, Rb and Cs respectively (Slater, 1965). These last figures agree with the radii of maximum radial charge density in the outermost shell of the alkali metals computed by Liberman, Waber & Cromer (1965) as 1.71, 2.16, 2.29 and 2.52 Å. It is remarkable that the inert gas potentials are qualitatively adequate to describe van der Waals non bonded interactions between S-S, Cl-Cl, Br-Br, I-I, Na⁺-Na⁺, K⁺-K⁺, Rb⁺-Rb⁺ and Cs⁺-Cs⁺. It seems likely, therefore, that the present approach may be extended to further atoms or ions.

In conclusion we believe that suitable atom-ion and ion-ion potentials are available to locate with sufficient accuracy the minima of the energy surface in crystals in order to solve the phase problem, at least for some simple cases. We propose to extend these calculations to more difficult biological crystal structures thus submitting these functions to a more severe test.

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The Prediction of Spot Positions on Equi-Inclination Weissenberg Photographs

BY J. A. D. JEFFREYS

Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow C. 1, Scotland

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An algorithm is presented for using equi-inclination Weissenberg and precession photographs to index an unknown triclinic cell to give a right-handed homogeneous vertex at the origin. Using such indexing, and known crystal parameters and camera settings, the geometry of reflexion is analysed to predict spot positions on both halves of equi-inclination Weissenberg photographs.

Introduction

The method for converting spot positions on a Weissenberg photograph into reciprocal-lattice coordinates has been fully described by Buerger (1942*a*). The converse operation of predicting spot positions on any one of a pack of films recording the intensities of the

n-layer is treated below. The orientation of the film both in the camera and after development, the camera design, and the axial labelling must be strictly defined if the treatment given is to apply. This assumes that both a Weissenberg and a precession camera are available, and it is limited to equi-inclination Weissenberg photographs.