

D'où une méthode algébrique de construction des groupes magnétiques associés à G_e : on recherche les extensions inéquivalentes de G' par T_k , on utilise dans ce but les relations entre générateurs de G' . On doit naturellement imposer: $T_{t,t} = 2t$.

Cette méthode permet en particulier de construire les groupes d'espace de réseau non primitif en les considérant comme extensions d'un groupe G' par un groupe de translations entières. Si on considère G_e comme extension de G par T , l'application de $G \times G$ dans T peut faire intervenir des translations de $(T-P)$; alors il n'existe pas de sous-groupe de G_e de réseau P et de classe G (en particulier s'il existe des miroirs d).

Conclusion

La méthode des représentations et la méthode directe de construction des groupes magnétiques s'appliquent au cas des groupes d'espace de réseau non primitif. On peut simplifier ces méthodes en se ramenant au cas des réseaux primitifs par la considération du groupe facteur $G' = G_e/P$.

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Van der Waals, Hydrogen Bonding, Ion-Dipole and Coulomb Energies in Crystals

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Some potentials describing electrostatic and ion-dipole interactions have been tested in known crystal structures for use in a general solution of the phase problem. Sodium tetrazolate monohydrate ($\text{Na}^+\text{HCN}_4^-\cdot\text{H}_2\text{O}$) has been considered to assess qualitatively the contribution of the various forces stabilizing the crystal lattice. In spite of the competitive effect among different energy terms the actual structure agrees satisfactorily with the deepest energy minimum. Sodium, potassium and rubidium azides (NaN_3 , KN_3 and RbN_3) have been investigated to obtain qualitative potentials for alkali ions and charged nitrogen atoms.

Introduction

Some potentials were previously verified in known crystal structures in order to assess the qualitative validity of semi-empirical functions for solving the phase problem. These potentials were used in calculations of packing energy which were performed by considering van der Waals, hydrogen bonding and electrostatic interactions (Coiro, Giglio & Quagliata, 1972, and references quoted therein).

The aim of this paper is to study further the use of potentials suitable to describe ion-dipole and ion-ion interactions. Sodium tetrazolate monohydrate (NaTW) and sodium, potassium and rubidium azides have been investigated. Electrostatic potentials between alkali ions and charged nitrogen atoms have been tested to continue a research programme concerning alkali ions and charged oxygen atoms (Capaccio, Giacomello &

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Giglio, 1971). Moreover the potential energy between sodium and tetrazolate ions and the permanent dipoles of the water molecules has been calculated neglecting the ion-induced dipole and ion-quadrupole terms, which are generally less important.

The semi-empirical potentials

The following interactions have been considered: NaTW: van der Waals, hydrogen bonding, ion-dipole, electrostatic; NaN_3 , KN_3 , RbN_3 : van der Waals, electrostatic.

The dipole-dipole energy among water molecules of NaTW has been computed in preliminary calculations by means of the relationship

$$V(r_{ab}, \theta_a, \theta_b, \varphi) = -14.393 \mu_a \mu_b r_{ab}^{-3} (2 \cos \theta_a \cos \theta_b - \sin \theta_a \sin \theta_b \cos \varphi)$$

where μ_a and μ_b represent two point dipoles at a distance r_{ab} apart, θ_a and θ_b are the angles formed by the vectors of magnitude μ_a and μ_b respectively with r_{ab} , and φ is the dihedral angle between the planes passing through μ_a, r_{ab} and μ_b, r_{ab} . V is in kcal if μ_a and μ_b are given in Debye units and r_{ab} in Å. However, this energy is not included in the results listed below because the position of the energy minima is insensitive to this contribution, which is comparatively very low.

The van der Waals coefficients of the atom-atom, atom-ion and ion-ion potentials in the generalized form:

$$V(r) = a \exp(-br)/r^d - cr^{-6}$$

are reported in Table 1. The potentials proposed by Mason & Rice (1954) and Kane (1939) for the two rare gases preceding and following the alkali metal in the periodic table have been tested for each ion, since they were satisfactorily employed for the same ion (Capaccio, Giacomello & Giglio, 1971) as well as for sulphur (Giglio, Liquori & Mazzarella, 1968), chlorine (Di Nola & Giglio, 1970), bromine and iodine atoms (Giglio, 1970). It should be noticed that the repulsive potential between the oxygen atom and the sodium ion in NaTW has been modified for short $\text{Na}^+ \cdots \text{O}$ distances when the $\text{O}-\text{Ar}^a$ potential of Table I is used. In fact, in this case there are experimental data to determine the $\text{Ar}-\text{Ar}^a$ coefficients for $r \leq 3$ Å. Then the repulsive term $\text{O}-\text{Ar}^a$ is obtained by averaging geometrically the repulsion parameters of the $\text{O}-\text{O}$ and $\text{Ar}-\text{Ar}^a$ functions.

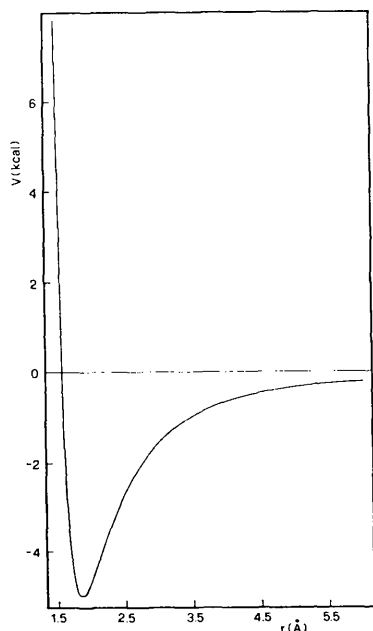


Fig. 1. Section of the hydrogen bonding $\text{O}-\text{H} \cdots \text{N}$ energy surface with $\theta_a = \theta_b = \varphi = 0^\circ$.

Table 1. The coefficients of the van der Waals potential functions

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

Interaction	$a \times 10^{-3}$	b	c	d
H—H	6.6	4.080	49.2	0
H—C	44.8	2.040	125.0	6
H—N	52.1	2.040	132.0	6
H—O	42.0	2.040	132.7	6
H—Ne ^a	26.2	4.344	78.5	0
H—Ne ^b	31.1	4.431	75.6	0
H—Ar ^a	40.5	3.851	265.2	0
H—Ar ^b	233.8	4.431	248.8	0
C—C	301.2	0.000	327.2	12
C—N	340.0	0.000	340.0	12
C—O	278.7	0.000	342.3	12
C—Ne ^a	188.6	2.304	202.3	6
C—Ne ^b	227.0	2.391	194.9	6
C—Ar ^a	255.4	1.811	684.0	6
C—Ar ^b	1677.6	2.391	641.7	6
N—N	387.0	0.000	354.0	12
N—O	316.2	0.000	356.0	12
O—O	259.0	0.000	358.5	12
O—Ne ^a	165.1	2.304	207.3	6
O—Ne ^b	202.8	2.391	203.9	6
O—Ar ^a	239.2	1.811	715.5	6
O—Ar ^b	1508.9	2.391	671.2	6
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	1430.0	0
Ar—Ar ^b	11954.5	4.782	1258.4	0
Kr—Kr ^a	65.8	3.033	2733.8	0
Kr—Kr ^b	31353.4	4.782	2132.9	0
Xe—Xe ^a	174.2	2.921	6626.0	0
Xe—Xe ^b	264991.4	4.782	5096.0	0

(a) Mason & Rice (1954).

(b) Kane (1939).

The potential proposed by Stockmayer (1941) for two polar gas molecules, successfully employed in the analysis of dimethylglyoxime (Giglio, 1969), diketopiperazine (Giacomello & Giglio, 1970) and N,N' -dicyclohexylurea (Coiro, Giacomello & Giglio, 1971), has been considered suitable to represent the formation of $\text{O}-\text{H} \cdots \text{N}$ hydrogen bonds between the water molecules and the tetrazolate anion in NaTW. This function can be written:

$$V(r, \theta_a, \theta_b, \varphi) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] - \mu_a \mu_b r^{-3}(2 \cos \theta_a \cos \theta_b - \sin \theta_a \sin \theta_b \cos \varphi)$$

The Lennard-Jones term gives the dispersion and the repulsive energy of the $\text{H} \cdots \text{N}$ interaction. The remaining term refers to the electrostatic energy between two point dipoles centred on H and N atoms and oriented along the $\text{O}-\text{H}$ bond and the NP segment, P being the centroid of the tetrazolate anion. The values of the parameters $\epsilon = 0.0016$ kcal, $\sigma = 2.94$ Å, $\mu_a \mu_b = 20.88$ kcal Å³ have been determined (Giglio, 1969) by putting $V = -5$ kcal and $\delta V / \delta r = 0$ when the O,H,N atoms and the P point are collinear and $r = 1.85$ Å. Since V is a slowly increasing function of r (see Fig. 1) an $\text{H} \cdots \text{N}$ cut-off distance of 2.5 Å has been introduced in the energy calculations.

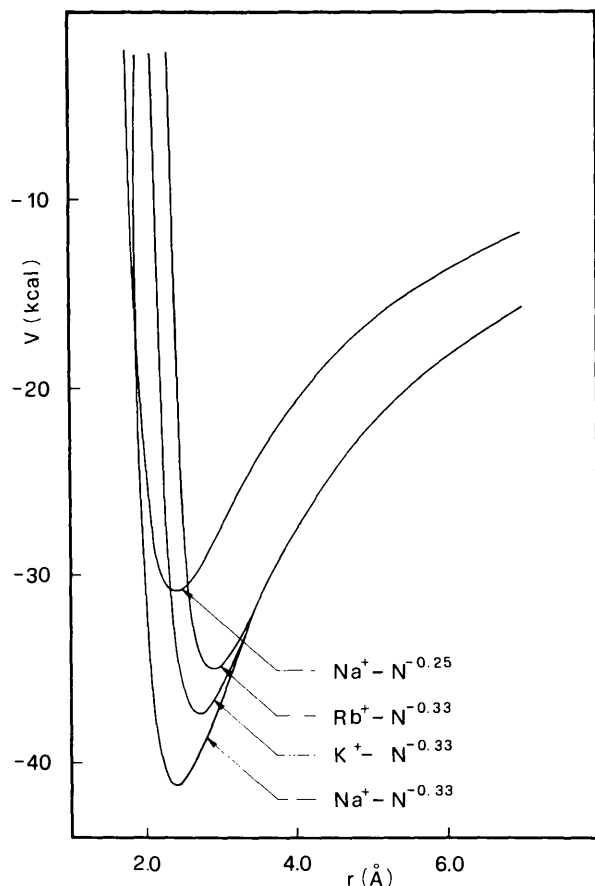


Fig. 2. Energy curves of the ionic alkali-nitrogen interactions. The ionic charges are reported in the Figure.

The ion-dipole potential energy of the permanent dipole μ of the water molecule in the field of the sodium or tetrazolate ion of charge e has been computed from

$$V(r, \varphi) = -e\mu \cos \varphi / r^2$$

where r is the distance between the ion and the midpoint of the dipole and φ is the angle the dipole makes with r . This equation is valid if the ratio between the length of the dipole and r is very small. The dipole moment of the water molecule has been assumed to be 1.84D (Eisenberg & Kauzmann, 1969) and the midpoint M of the dipole has been taken on the bisector of the HOH angle at 0.3 Å from the oxygen atom.

The ion-ion potential function

$$V(r) = Z^+ Z^- / r + a \exp(-br)$$

containing a Coulombic term and a two-parameter repulsive potential has been used for describing the alkali ion-nitrogen interactions (Capaccio, Giacomello & Giglio, 1971). Here r is the interionic distance and Z^+ and Z^- the effective ionic charges, which have been taken as unity except for the nitrogen atoms ($Z^- = -0.33$ and -0.25). Since experimental data concerning the constant b are lacking, this parameter has been

varied over a reasonable range. Thus, with a given value of b , the coefficient a has been evaluated by minimizing the complete function at a distance r_m chosen from the literature, considering the shortest contacts in

Table 2. Coefficients of the ionic alkali-nitrogen potentials

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

Interaction	$Z^+ Z^-$ (kcal Å)	a (kcal/ ion-pair)	b (Å ⁻¹)	r_m (Å)
Na-N	-82.88	53109	4.0	2.4
Na-N	-110.50	70812	4.0	2.4
K-N	-110.50	497279	4.4	2.7
Rb-N	-110.50	1039229	4.4	2.9

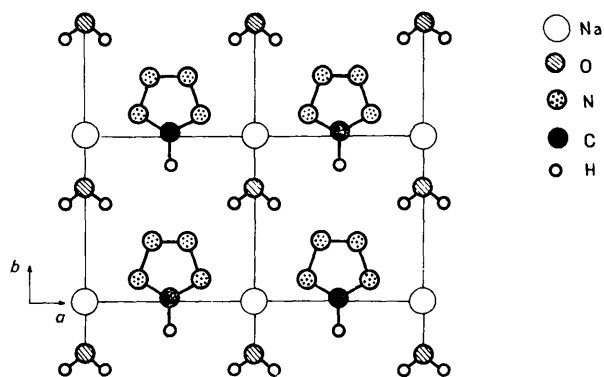


Fig. 3. Packing of NaTW viewed along c . The sodium ions are at $z=0$ and the remaining atoms at $z=\frac{1}{2}$.

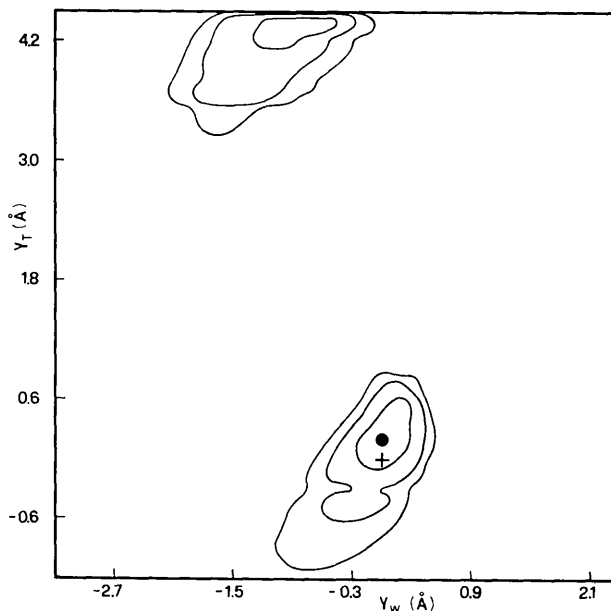


Fig. 4. Potential energy in the crystal of NaTW as a function of Y_w and Y_t . Contours are drawn at arbitrary intervals. The black spot corresponds to the deepest minimum and the cross to the actual structure.

real structures. The best ion-ion energy curves found are reported in Fig. 2 and the corresponding coefficients are listed in Table 2. The electrostatic energy of ions with the same polarity has been computed by means of the simple Coulomb equation.

Sodium tetrazolate monohydrate

This compound crystallizes in the space group $Pmcm$, with $a=5.868$, $b=5.624$, $c=6.450$ Å; $Z=2$ (Palenik,

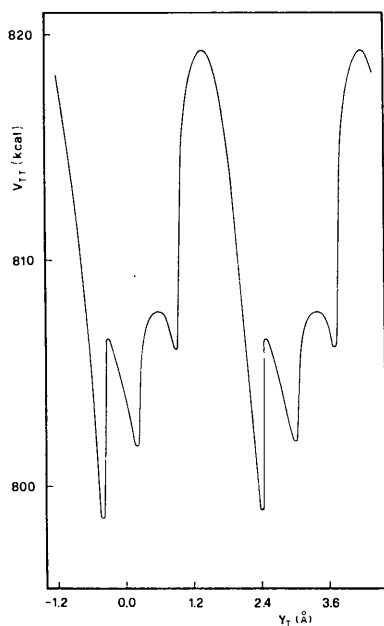


Fig. 5. Electrostatic and van der Waals energy T-T vs. Y_T .

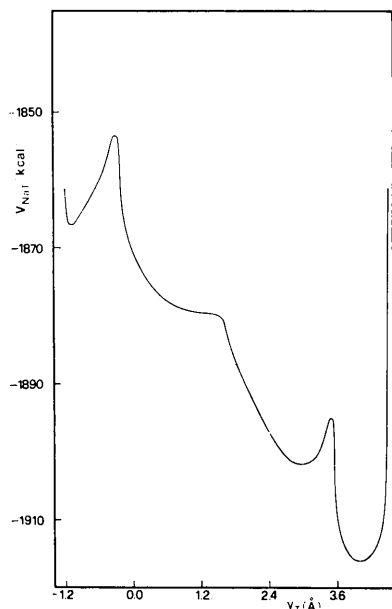


Fig. 6. Electrostatic and van der Waals energy Na-T vs. Y_T .

1963). A view of the crystal packing down c is shown in Fig. 3. The sodium ions, the oxygen atoms and the centroid P of the tetrazolate anions are in the special positions:

$$\begin{aligned} \text{Na: } & 2(a) (0,0,0; 0,0,\frac{1}{2}) \\ \text{O: } & 2(e) (0,y,\frac{1}{4}; 0,-y,\frac{3}{4}) \\ \text{P: } & 2(f) (\frac{1}{2},y,\frac{1}{4}; \frac{1}{2},-y,\frac{3}{4}). \end{aligned}$$

There are two translational degrees of freedom along b , one of the water molecule (Y_w) and the other of the tetrazolate anion (Y_T). The atomic coordinates determined by Palenik (1963) have been employed in the calculations except those of the hydrogen atoms (see Table 3) because the limit of error in the hydrogen positional parameters is very high. The O-H and C-H bond lengths were assumed to be 1.00 and 1.08 Å respectively and the HOH angle 105°.

Table 3. Atomic coordinates (Å) used in the calculations and corresponding to $Y_T = Y_w = 0$ Å

For the points P and M see text.

	x	y	z
Na	0.0000	0.0000	0.0000
N ₁	1.8296	0.7778	1.6125
N ₂	2.2791	2.0488	1.6125
N ₃	4.0384	0.7778	1.6125
N ₄	3.5889	2.0488	1.6125
C	2.9340	0.0388	1.6125
H ₁	2.9340	-1.0312	1.6125
O	0.0000	3.8356	1.6125
H ₂	0.7934	3.2268	1.6125
H ₃	-0.7934	3.2268	1.6125
P	2.9340	1.1384	1.6125
M	0.0000	3.5312	1.6125

The potential energy has been computed as a function of Y_w and Y_T with translational increments of 0.3 Å in the first run and of 0.1 Å in the last minimum search. All interactions have been evaluated for a set of molecules consisting of a central one and the fourteen closest neighbours. The negative charge of the tetrazolate anion has been equally distributed over the nitrogen atoms ($Z^- = -0.25$). It is possible that the two nitrogen atoms nearer to the cation (see Fig. 3) have a slight excess of negative charge. However, calculations performed with Z^- equal to -0.3 and -0.2 for the nitrogen atoms closer to and farther from the sodium ion gave practically the same result.

Two minima A and B, noticeably lower than the others, are shown in Fig. 4, where the black spot represents the absolute minimum (A) and the cross the experimental structure. In this and in the following Figures the van der Waals and electrostatic interactions involving the sodium ions have been described by the potential Ne-Ne^b of Table 1 and by the first potential of Table 2. It is interesting to divide each asymmetric unit into sodium ion (Na), tetrazolate anion (T) and

water molecule (W) and to present the energy values, which refer to the interactions between two of these chemical species, as a function of Y_W and Y_T (see Figs. 5–10). The data of the minima *A* and *B* are reported in Table 4. Since V_{NaNa} is constant (1305.3 kcal) it is omitted in the estimate of the total energy (V_{Tot}).

The deepest minimum *A* corresponds satisfactorily to the experimental structure and is insensitive to a large range of the repulsion parameter b of the Na–N electrostatic interaction. The Ne–Ne van der Waals potentials give slightly better results than the Ar–Ar ones of Table 1. The shape of the minimum *A* shows that the potential-energy gradient along \mathbf{b} is lower for the tetrazolate anion than for the water molecule. This is supported by the final B_{22} thermal parameters (Palenik, 1963) which are greater for carbon and nitrogen than for oxygen.

Sodium, potassium and rubidium azides

NaN_3 (Hendricks & Pauling, 1925) is rhombohedral, space group $R\bar{3}m$, with a trimolecular hexagonal cell and $a = 3.637$, $c = 15.209$ Å.

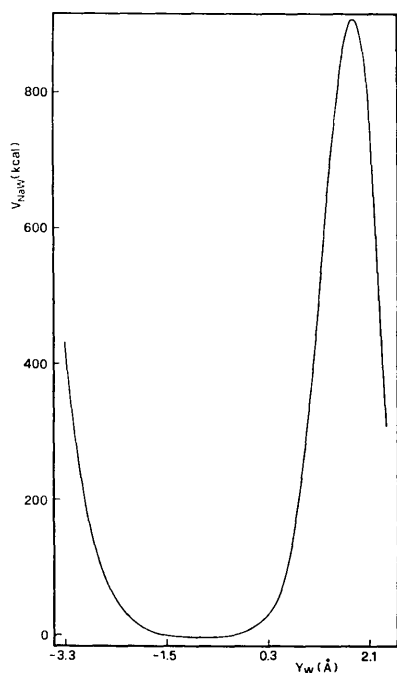


Fig. 7. Van der Waals energy Na–W vs. Y_W .

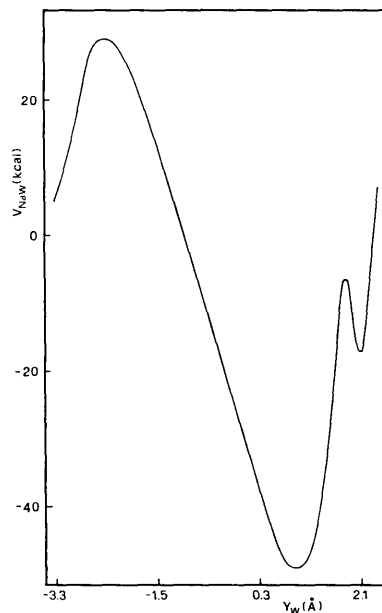


Fig. 8. Ion-dipole energy Na–W vs. Y_W .

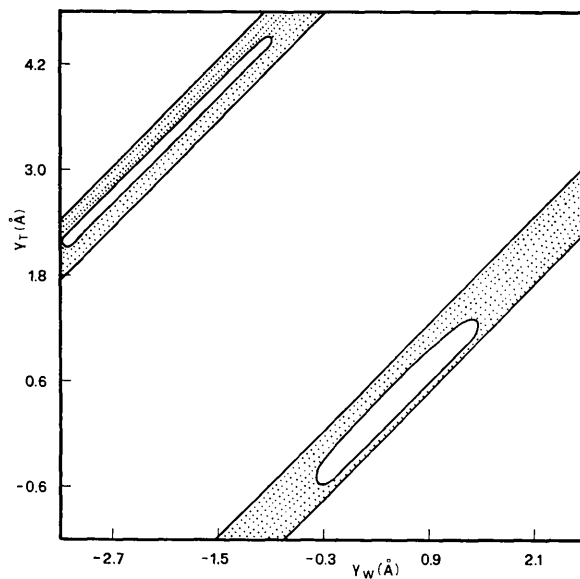


Fig. 9. Van der Waals energy T–W as a function of Y_W and Y_T . The first contour corresponds to -5 kcal and the dotted areas include values in the range -5 to -3 kcal.

Table 4. Values of the energy terms (kcal) relative to the *A* and *B* minima

V_{HIB} is the stabilization energy of the hydrogen bonds between T and W and is not included in V_{TW}

	Y_T (Å)	Y_W (Å)	V_{NaT}	V_{NaW}	V_{TT}	V_{TW}	V_{HIB}	V_{WW}	V_{Tot}
<i>A</i>	0.2	0.0	-1874.1	-21.1	801.8	-19.7	-12.4	-1.0	-1126.5
<i>B</i>	4.4	-0.8	-1910.9	-6.9	818.4	-9.2	-11.0	-1.1	-1120.7

If N_0 is the central nitrogen atom of the linear N_3 ion, the atoms are in the positions:

$$\begin{aligned} \text{Na: } & 3(a) (0, 0, 0) \\ \text{N}_0: & 3(b) (0, 0, \frac{1}{2}) \\ \text{N: } & 6(c) (0, 0, z; 0, 0, -z) \end{aligned}$$

KN_3 and RbN_3 (Pauling, 1930) have $Z=4$ and

$$\begin{aligned} a &= 6.094, c = 7.056 \text{ \AA}; \\ a &= 6.36, c = 7.41 \text{ \AA}; \end{aligned}$$

respectively. The atoms are in the following special positions of the space group $I4/mcm$

$$\begin{aligned} \text{K (or Rb): } & 4(a) (0, 0, \frac{1}{4}; 0, 0, \frac{3}{4}) \\ \text{N}_0: & 4(d) (0, \frac{1}{2}, 0; \frac{1}{2}, 0, 0) \\ \text{N: } & 8(h) (x, \frac{1}{2} + x, 0; -x, \frac{1}{2} - x, 0; \frac{1}{2} + x, -x, 0; \\ & \frac{1}{2} - x, x, 0). \end{aligned}$$

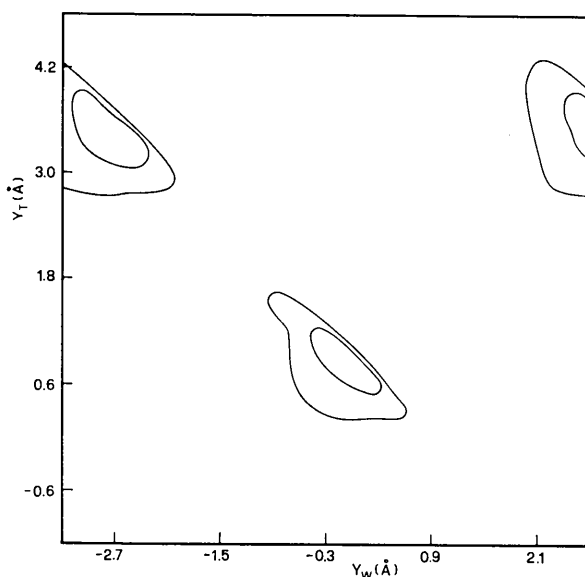


Fig. 10. Ion-dipole energy $T-W$ as a function of Y_w and Y_r . Contours are drawn at -20 and -15 kcal.

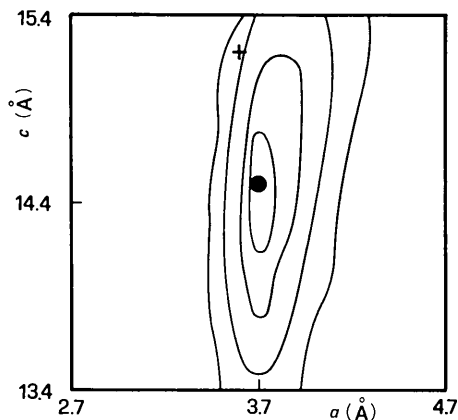


Fig. 11. Potential energy of NaN_3 computed as a function of a and c with the Ne-Ne^b potential. Contours are drawn at arbitrary interval.

If both N-N bond lengths are fixed at 1.15 \AA all the parameters are determined. Thus the potential energy has been evaluated as a function of the unit-cell edges a and c by taking into account van der Waals and Coulomb interactions between one asymmetric unit and the twelve (NaN_3) and fourteen (KN_3 and RbN_3) nearest ones. A charge of -0.33 has been assigned to each nitrogen atom. Similar calculations have been carried out varying the charge of N_0 from -0.33 to 0 and those of the outer nitrogen atoms from -0.33 to -0.5 . The positions of the minima are only very slightly altered.

The potentials used are those of Tables 1 and 2 and the final increment is 0.1 \AA in the minimum energy search. The results obtained for NaN_3 , KN_3 and RbN_3 are summarized in Table 5, where the percentage error is defined as: $\Delta a/a = (a_{\text{calc}} - a_{\text{obs}})/a_{\text{obs}}$ and likewise for $\Delta c/c$. The inert-gas potential employed in describing the van der Waals interactions of the cation is reported in the first column of Table 5. The shapes of the energy minima are shown in Figs. 11-13, where the cross and the black spot represent the actual structure and the calculated deepest minimum respectively. These calculations have been repeated with different repulsion parameters over a large range. The agreement with the experimental data is generally better if $b \geq 4.0 \text{ \AA}^{-1}$ for NaN_3 and RbN_3 and $b \geq 4.4 \text{ \AA}^{-1}$ for KN_3 .

Table 5. Values of the parameters a and c and percentage errors corresponding to the lowest minima found in the analyses of NaN_3 , KN_3 and RbN_3

Potential	Compound	a (\AA)	$\Delta a/a$ (%)	c (\AA)	$\Delta c/c$ (%)
Ne-Ne ^a	NaN ₃	3.7	1.6	14.5	-4.7
		3.7	1.6	14.5	-4.7
		3.8	4.4	14.6	-4.0
		3.8	4.4	14.6	-4.0
Ar-Ar ^a	NaN ₃	3.8	4.4	14.6	-4.0
		3.8	4.4	14.6	-4.0
		3.8	4.4	14.6	-4.0
		3.8	4.4	14.6	-4.0
Kr-Kr ^a	KN ₃	6.2	1.8	6.9	-2.3
		6.3	3.4	6.9	-2.3
		6.2	1.8	6.9	-2.3
		6.2	1.8	7.0	-0.8
Kr-Kr ^b	KN ₃	6.2	1.8	6.9	-2.3
		6.2	1.8	7.0	-0.8
		6.2	1.8	7.0	-0.8
		6.2	1.8	7.0	-0.8
Xe-Xe ^a	RbN ₃	6.6	3.8	7.2	-2.8
		6.6	3.8	7.3	-1.5
		6.6	3.8	7.5	1.2
		6.5	2.2	7.7	3.9

(a) Mason & Rice (1954).

(b) Kane (1939).

Discussion

Inspection of Table 4 shows that the actual molecular arrangement in the crystal of NaN_3 is favoured by the ion-dipole energy, which is included in V_{NaW} and V_{TW} . On the other hand the minimum B , in comparison with A , is stabilized by the electrostatic energy V_{NaT} and V_{TT} . Thus these energies are competitive in making deeper A and B and the ion-dipole energy prevails. However, it must be stressed that the interaction dominating the $\text{Na}^+ \cdots \text{H}_2\text{O}$ bonding is the repulsive one, which occurs at short distances in the minimum zones.

Thus the corresponding energy is quantitatively inaccurate.

With regard to the various forces taken into account in the analysis of NaTW it has to be mentioned that the more important energy terms do not contribute in the best way for lowering A (see Figs. 5-10). Nevertheless the competitive effects of these forces can be qualitatively accounted for by means of semi-empirical potentials even though a quantitative treatment is precluded. Moreover the effective values both of the ionic charges and of the dielectric constant for every electrostatic interaction are unknown in NaTW as well as in alkali azide crystals. Fortunately the positions of the minima are only slightly sensitive to the changes of the ionic charges, and the dielectric constant can be taken as unity if only the interactions between one asymmetric unit and the first shell of asymmetric units are considered. The inclusion of further shells gives rise to worse agreement as was the case for other crystals containing sodium, potassium, rubidium, caesium and oxygen ions (Capaccio, Giacomello & Giglio, 1971). A comparison of the results obtained in this paper and in Capaccio *et al.* (1971) with different noble-gas potentials shows that the Kr-Kr and Xe-Xe functions of Kane (1939) give better results for potassium and rubidium in all the compounds studied. On the contrary sodium is more satisfactorily described by Ne-Ne potentials in NaTW and NaN_3 and by Ar-Ar potentials in sodium oxalate and formate.

In conclusion it is noteworthy that the rare-gas potentials are qualitatively adequate to represent the van der Waals interactions of neutral or charged atoms with nearly equal atomic numbers. It seems reasonable,

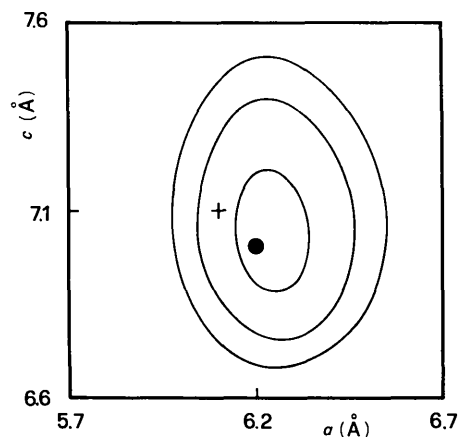


Fig. 12. Potential energy of KN_3 computed as a function of a and c with the Kr-Kr^b potential. Contours are drawn at arbitrary intervals.

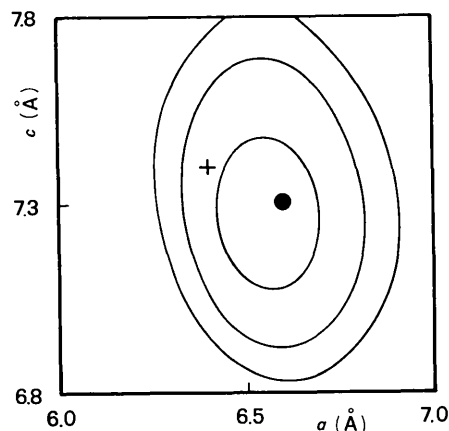


Fig. 13. Potential energy of RbN_3 computed as a function of a and c with the Kr-Kr^b potential. Contours are drawn at arbitrary intervals.

therefore, to employ these or very similar functions for charged or neutral atoms belonging to the second, fifth and sixth groups of the periodic table (Giglio, 1970). In addition it is hoped that the potentials tested by us will be suitable to solve the phase problem even though several kinds of forces are present.

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