Acta Cryst. (1961). **14**, 547

Crystal radius of the cyanide ion.

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(*Received* 14 *November* 1960)

Although the cyanide ion is non-spherical it can attain effective spherical symmetry by free rotation in certain crystals. Thus at ordinary temperatures NaCN, KCN, and RbCN crystallize with the rock-salt structure and CsCN crystallizes with the caesium chloride structure. The effective radius of the cyanide ion is about 1·92 Å and may be taken as being essentially constant. This is shown by a comparison of measured unit-cell lengths and corresponding lengths calculated using 1·92 Å as the radius of CN^- and Pauling's crystal radii for alkali metal ions.

	NaCN	KCN	RbCN	CsCN
a_0 (obs.)	5·89 Å	6·51 Å	6·82 Å	4·25 Å
a_0 (calc.)	5·87	6·51	6·79	4·26

In deriving the values of a_0(calc.) the effect of radius ratio and coordination number on interionic distance has been taken into account (Pauling, 1960).

The crystal radius assigned to the cyanide ion may be used for the estimation of the lattice energies of sodium cyanide and potassium cyanide. The lattice energy U of a crystal MX at 298·16 °K. and the enthalpy of hydration H of the gaseous ions M^+ and X^- are related by the equation

$$U = -H + S - 596{\cdot}32R\,, \qquad (1)$$

where S is the standard enthalpy of solution of the crystalline compound and R is the gas constant. Since the lattice energies of alkali halides are accurately known, the standard enthalpy of hydration of pairs of alkali and halide ions can be determined from equation (1). If these enthalpies of hydration are plotted against the reciprocals of the Pauling crystal radii of halide ions, parallel straight lines are obtained (Fig. 1). Using the value for the ionic radius of CN^- it is possible to obtain $-H$ for $(Na^+ + CN^-)$ and $(K^+ + CN^-)$ by interpolation from the plots. The lattice energies of NaCN and KCN may then be obtained from equation (1) using data for the heats of solution of the compounds from the National Bureau of Standards Circular (Rossini *et al.*, 1952). Results for the lattice energies are shown in Table 1 in comparison with recent theoretically calculated values due to Waddington (1959) and Ladd & Lee (1960); older values due to Sherman (1932) are also listed. The consistency of the calculated lattice energies may be tested by using them in the derivation of the enthalpy of formation of the gaseous cyanide ion by means of the equation

$$\Delta H^0_{298}(CN^-g) = U + 596{\cdot}32R - \Delta H^0_{298}(M^+g) + \Delta H^0_{298}(MCNc)\,. \qquad (2)$$

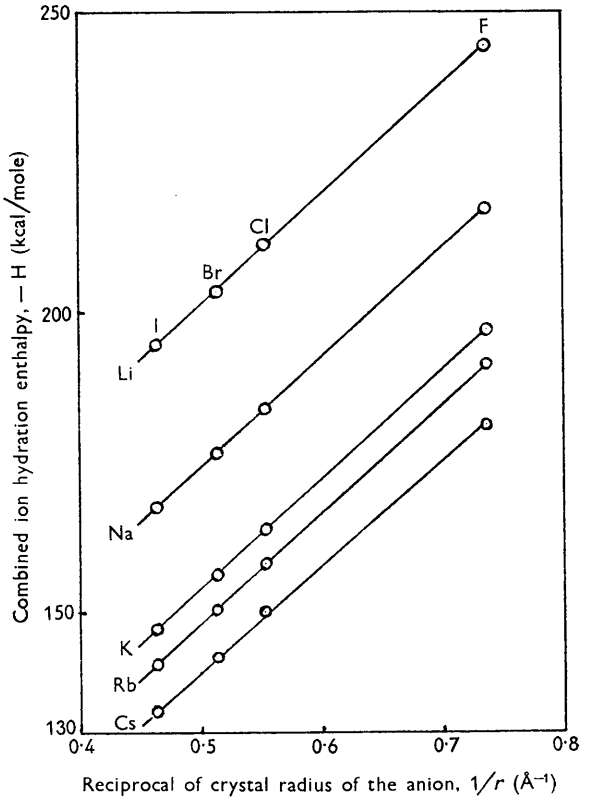

Fig. 1. Enthalpies of hydration as functions of anion radii.

Table 1. *Lattice energies of alkali metal cyanides*

(Values in kg.cal./mole)

	Present work		Ladd & Lee (1960)		Waddington (1959) (i) Using simple Born–Mayer equation		Waddington (1959) (ii) Using treatment of Huggins (1937)		Waddington (1959) (iii) Using the equation of Kapustinskii (1943) with 'thermochemical radius' for CN^- due to Yatsimirskii (1947)		Sherman (1932)	
Salt	U	$\Delta H^0_{298}(CN^-g)$	U	$\Delta H^0_{298}(CN^-g)$	U	$\Delta H^0_{298}(CN^-g)$	U	$\Delta H^0_{298}(CN^-g)$	U	$\Delta H^0_{298}(CN^-g)$	U	$\Delta H^0_{298}(CN^-g)$
LiCN									192			
NaCN	177·0	10·7			174	7·7	170·2	3·9	179	12·7	169·4	3·1
KCN	159·4	10·6	161	13	158	9·2	156·5	7·7	162	13·2	154·9	6·1
RbCN					151	8·4	150·3	7·5	155	12·2	149·1	6·3
CsCN					139	3·3	142·4	7·7	149	13·3	141·3	6·6

Taking the value of $\Delta H^0_{298}(CN^-g)$ as 10·6 kg.cal./mole and $\Delta H^0_{298}(CNg)$ as 92 kg.cal./mole (Skinner, 1958), the electron affinity of the cyanide radical $E_{298}(CN)$ is found to be 81·4 kg.cal./mole. This value for the electron affinity is probably reliable to within ±3 kg.cal.

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Acta Cryst. (1961). **14**, 548

The lattice constants of orthorhombic sulfur and revision of the interatomic distances.

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(*Received* 18 *November* 1960)

As a part of his careful refinement of the parameters in orthorhombic sulfur, Abrahams (1955) also redetermined the lattice constants from precession photographs corrected for film shrinkage. The values he obtained are:

$$a = 10{\cdot}437,\ b = 12{\cdot}845,\ c = 24{\cdot}369\ \text{Å},\ \text{all}\ \pm 0{\cdot}010\ \text{Å}$$

(at room temperature). These values give a calculated density of 2·086 g.cm.$^{-3}$. Swanson *et al.* (1960), hereinafter called NBS, have recently reported significantly different values, namely,

$$a = 10{\cdot}468,\ b = 12{\cdot}870,\ c = 24{\cdot}49\ \text{Å}\ ,$$

at 25 °C. These were obtained by a least squares treatment of resolved lines in the latter half of the powder pattern as recorded with a Geiger counter diffractometer. The standard errors were not given. The corresponding calculated density is 2·065 g.cm.$^{-3}$, in far better agreement with the observed value of 2·069 g.cm.$^{-3}$ (Batuecas & Losa, 1951), a fact highly suggestive that the earlier values were subject to systematic error.

As a check on the values reported by NBS, and to obtain a measure of their precision, we have reexamined their data, and have obtained, by least squares, the following values:

$$a = 10{\cdot}467 \pm 0{\cdot}001,\ b = 12{\cdot}870 \pm 0{\cdot}001\ ,$$
$$c = 24{\cdot}493 \pm 0{\cdot}003\ \text{Å}$$

(at 25 °C.). These values were obtained in the following way: (i) The lattice constants of NBS were used to calculate values of $\sin\theta/\lambda$ for all reflections within the Cu $K\alpha$ sphere; (ii) values of pF_o^2 were calculated from the single crystal data of Abrahams; (iii) all of the lines observed by NBS were assigned indices on the basis of (i) and (ii); (iv) data for lines which clearly were not unresolved multiplets were then treated by least squares to obtain values for the lattice constants, and their standard errors. This treatment made use of 60 resolved lines. A drift correction was not used because no drift was found upon comparison of observed and calculated spacings. Our indexing is not always the same as that of NBS as shown in Table 1, which lists all lines where the indexing differs, regardless of whether the line was included in the least squares. It thus appears that their treatment omitted some lines which could have been included, and vice versa. It is interesting that although exactly the same data were not used by us and by NBS, the resulting values for the lattice constants are sensibly the same, due to compensating errors. The very small standard errors of the revised lattice constants do not, of course, include any systematic errors in their experiment, but the high standard of accuracy which characterizes the work from that laboratory together with the much better agreement that the revised lattice constants give with the experimental density leaves little doubt that they are in fact more accurate than those of Abrahams, or, for that matter, than those of earlier investigators cited by NBS.

Abrahams (1961) has very recently reported new values for the positional parameters as obtained from a least squares treatment which allowed for thermal anisotropy. These new parameters differ by an average of 0·004 Å from the old, and the average S–S bond distance changes from 2·037 Å to 2·041 Å. The present revision of the lattice constants leads to the following revised values of the molecular constants:

Bond lengths		Bond angles		Torsion angles	
S_1–S_3	2·046 Å	S_1'–S_1–S_3	108° 13′	S_1–S_3–S_2–S_4	101° 6′
S_2–S_3	2·050	S_3–S_2–S_4	107° 58′	S_1'–S_1–S_3–S_2	99° 7′
S_2–S_4	2·048	S_1–S_3–S_2	107° 11′	S_3–S_2–S_4–S_4'	98° 3′
S_1–S_1'	2·044	S_4'–S_4–S_2	108° 54′	S_3–S_1–S_1'–S_3'	97° 19′
S_4–S_4'	2·052			S_2–S_4–S_4'–S_2'	95° 1′
Av. 2·048 ± 0·002$_4$		107° 54′ ± 36′		98° 37′ ± 2° 9′	

The quoted uncertainties are standard errors as calculated on the assumption that we are looking at several measurements of the same quantity, with values involving the primed atoms being given half weight. The angular