

# The Crystal Structure of Dipotassium Ethylenetetracarboxylate

BY SURENDER KUMAR KUMRA

*College of Science and Technology, Manchester, England and Hans Raj College, Delhi, India*

AND S. F. DARLOW

*College of Science and Technology, Manchester, England*

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Dipotassium ethylenetetracarboxylate crystallizes in the orthorhombic space group  $Pbca$ , with 4 molecules per unit cell and cell dimensions

$$a = 9.724 \pm 0.015, b = 6.440 \pm 0.002, c = 14.175 \pm 0.007 \text{ \AA}.$$

A solution was obtained in projection by the use of Buerger's Minimum Function. The least-squares refinement of the three-dimensional data with anisotropic temperature parameters for all atoms except hydrogen brought the residual down to 10.4%.

The structure consists of alternate layers of cations and anions. The anions are so oriented that there are layers of oxygens on either side of the layers of potassium. The potassium atoms are arranged in an approximately square array and there is an intermolecular hydrogen bond of length  $2.514 \pm 0.011 \text{ \AA}$ .

## Introduction

The crystal structure of  $K_2^+ [C(COOH)COO]_2^-$  was investigated to determine the configuration of the anion for comparison with the hydrogen maleate anion

in potassium hydrogen maleate, whose structure has been reported by Darlow & Cochran (1961) and Darlow (1961). The two anions are shown in Fig. 1.

The hydrogen maleate anion (II) is completely planar, with a strong internal symmetrical hydrogen bond. The strain in the ring is mainly taken up by the angles marked \* increasing above their normal values. Anion (I), however, is almost double anion (II), and the angles cannot increase so easily. This structure was investigated to determine whether the anion (I) is planar or whether the strain is so great that the planarity is lost by rotation of the carboxyl groups, and to determine the hydrogen bonding.

## Experimental

A small amount of the specimen was provided in the powdered form by Dr P. C. Crofts of the Chemistry Department, College of Science and Technology, Manchester. The slow evaporation of its aqueous solution yielded thin plate-like crystals possessing orthorhombic symmetry. The cross-section of the crystals perpendicular to the  $[001]$  axis is a parallelogram with the shortest axis along the longer diagonal. The unit-cell sides as obtained from the rotation photographs were

$$a = 9.75, b = 6.42, c = 14.20 \text{ \AA}.$$

The density of the crystals was determined by flotation in a mixture of methyl iodide and ethanol and the mean of four independent observations was found to be  $2.095 \pm 0.005 \text{ g.cm}^{-3}$ .

The chemical composition of the crystals was not

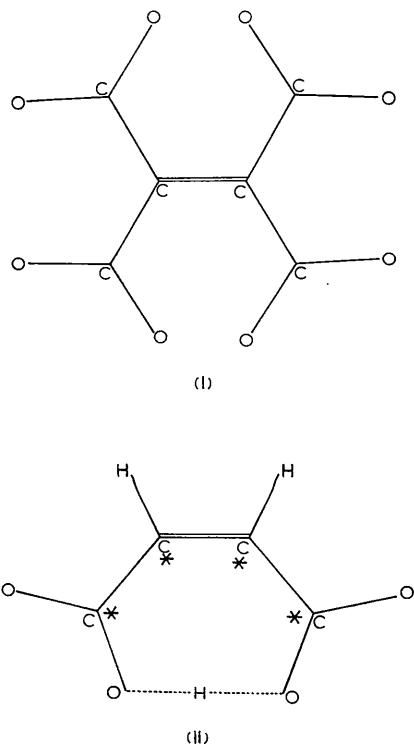


Fig. 1. (I) The divalent anion of ethylenetetracarboxylic acid.  
(II) The hydrogen maleate anion.

certain at the start but could be  $C_6H_2K_2O_8$  or  $C_6H_3KO_8 \cdot H_2O$ . The molecular weights in the two cases are 280 and 260 respectively. In either case the number of molecules per unit cell is 4. The above crystal data gave the molecular weight as  $283 \pm 4$  thus indicating that the chemical composition was  $C_6H_2K_2O_8$ .

Weissenberg normal beam and equi-inclination photographs showed the following systematic absences:  $h0l$  for  $l$  odd,  $0kl$  for  $k$  odd,  $hk0$  for  $h$  odd, ( $h00$  for  $h$  odd,  $0k0$  for  $k$  odd,  $00l$  for  $l$  odd). A closer examination of all the photographs showed six other spots not expected from the above rules with indices 010, 015, 017, 035, 039 and 0313. All of them were weak sharp spots, three of them being almost undetectable. If these six out of a possible 62 reflexions on the  $0kl$  film were genuine the space group would be  $P2_1ca$  or  $Pmca$ , but if they were Renninger reflexions the space group would be  $Pbca$ . The Howells, Phillips & Rogers test (1950) as applied to the  $h0l$  intensity data indicated that the space group is centrosymmetric and thus limited the possibilities to  $Pmca$  and  $Pbca$ . The analysis was carried out on the assumption that the extra reflexions were Renninger reflexions, there being intense reflexions which could account for them, and this was confirmed by the solution and subsequent refinement of the structure.

In the space group  $Pbca$  there are eight general equivalent positions, and there being only four molecules per unit cell the centre of each molecule must lie at a special position, with the two halves of the molecule lying symmetrically disposed about it.

The  $0kl$  and  $h0l$  intensity data were collected on a Weissenberg camera with Ni-filtered Cu  $K\alpha$  radiation at the normal beam setting using the multiple film technique. The intensities were estimated visually by comparison with a calibrated wedge and Lorentz and polarization corrections applied. There being only one good crystal it was not considered worth the risk to change its shape in order to determine the exact absorption correction. Therefore no correction was applied at the time of the two-dimensional analysis.

### Solution of the structure

The coordinates of the potassium atoms were found from the (100) and (010) Patterson projections. Minimum function maps ( $M_4$ ) (Buerger, 1951) for these projections (Fig. 2) were obtained from sharpened Patterson functions. Using the fact that the centre of the C=C bond must lie at a centre of symmetry, the atoms of the molecule were easily identified in the (010) projection and their positions checked by the optical transform match with the weighted reciprocal lattice. More difficulty was experienced in the (100) projection, but the initial trial structure for the (010) and (100) projections gave starting residuals of 33% and 31%. After two cycles of Fourier refinement, the rest of the refinement was carried out by

difference methods using reflexions for which  $\sin \theta/\lambda \geq 0.35$ . The residuals were reduced to 10.2% in seven cycles for the  $h0l$  data and to 12% in nine cycles for the  $0kl$  data.

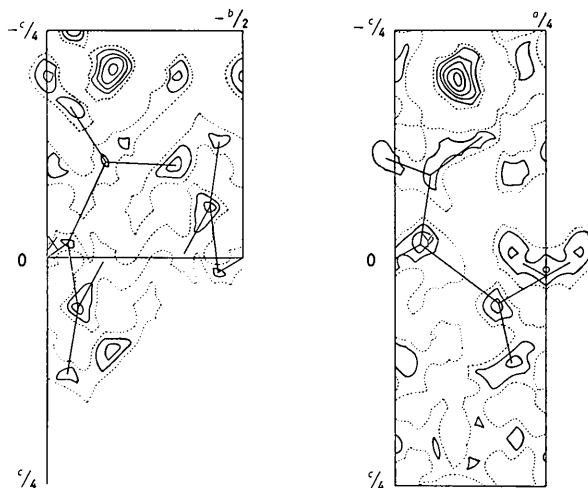


Fig. 2.  $M_4$  function for the (100) and (010) projections. The zero contour is dotted.

The difference maps indicated the need of anisotropic thermal parameters for K in the (010) projections and K, O(2) and O(4) in the (100) projections, and different isotropic thermal parameters for the rest of the atoms. The position of the hydrogen could not be found with certainty in either projection though it could be guessed from a study of all the O-O contacts. This is probably because the intensity data had not been corrected for absorption and the hydrogen atom contributes only to the low angle reflexions for which the variation in the correction is also a maximum. There was only one short O-O contact, of approximately 2.5 Å, and this was taken to be an intermolecular hydrogen bond between the pair of atoms O(1) and O(3).

The rest of the refinement was carried out with the full range of data with the minimum residual technique described by Bhuiya & Stanley (1963). In the two stages of minimum residual refinement the residual of the  $h0l$  data fell to 8.9% and 7.9% and that of the  $0kl$  data to 8.9% and finally 8.3%.

### Three-dimensional refinement

The crystal that had been employed for the two-dimensional analysis was also used for collecting the data for the three-dimensional refinement. The  $1kl, 2kl, \dots, 6kl$  intensity data were collected at the equi-inclination setting and the spot-shape correction given by Phillips (1956) applied to the elongated spots. The contracted spots were empirically scaled to these corrected intensities. For the purpose of calculating the absorption correction, using a Mercury

Autocode Program written by Dr Woolfson, the dimensions of a simpler crystal that would cause nearly the same absorption as the actual crystal were estimated and the correction applied to the full intensity data. The 'simpler crystal' was a rectangular parallelepiped with dimensions 0.16, 0.25 and 0.07 mm, and  $\mu = 98.5 \text{ cm}^{-1}$ .

The layers of the observed structure factors were on different scales, and were put on the same scale by scaling the intensity data of each layer with the calculated structure factors. The structure was refined by use of the least-squares program of Dr J. S. Rollett. Only the anisotropic refinement was carried out. The weighting scheme adopted was

$$w = 1/(1 + (F_o/b)^2)$$

and the constant  $b$  was given the value 2, the average  $F_{\min}$  being 1.3.

Though the position of the hydrogen atom could be guessed from the results of the two-dimensional analysis, it was not included in the refinement in the initial stages and instead the refinement was carried out with the 437 moderate and high angle reflexions only ( $\sin \theta/\lambda \geq 0.35$ ). Hydrogen makes very little contribution to these reflexions and it was thought that when at a later stage the hydrogen was included and the refinement carried out with the full data it would not cause much disturbance to the course of the refinement.

Six cycles of refinement were carried out, the residual starting at 14.8%. In general the indicated parameter changes were too large, probably owing to the effect of the absent reflexions (Cruickshank, 1956). The hydrogen was then included half-way along O(1) ··· O(3) and the refinement continued with the full data. In another two cycles the residual dropped to 11.3%. In order to allow for the absent reflexions, the procedure proposed by Smare (1948) and followed

by numerous workers, notably Truter, Cruickshank & Jeffery (1960) and Truter (1960), was followed with a slight modification. An estimate was made of the minimum  $F_o$  which could have been observed in that range of  $\sin \theta$  and, for refinement, the expected value of  $F_o$  was taken as  $\frac{1}{2}F_{\min}$  only for those reflexions whose calculated structure factors at this stage were greater than  $\frac{1}{6}F_{\min}$ . Another two cycles of least-squares refinement brought the residual of the full data down to 10.4%. The final positional coordinates and the  $b_{ij}$  values of the different atoms are given in Tables 1 and 2. The observed and calculated  $F$  values are listed in Table 8.

For the hydrogen the isotropic temperature parameter  $B = 2.1 \text{ \AA}^2$  was assumed. These  $b_{ij}$  values were not analysed further, and no libration corrections have been applied to the bond lengths.

### Estimation of errors

The standard deviations of the positional coordinates were estimated with the use of Cruickshank's relationship (1960). For the  $x$  coordinates a correction was made for the fact that the data in this direction had not been collected to the edge of the Cu  $K\alpha$  sphere. The r.m.s. value of the reciprocal radius adopted for the purpose exceeded the value for the highest layer line by an amount proportional to the ratio of the  $h0l$  reflexions included in the refinement to the total number.

The standard deviations of the various atoms thus obtained were:

Atom	$\sigma(x)$	$\sigma(y) = \sigma(z)$
K	0.004 Å	0.002 Å
O	0.009	0.005
C	0.015	0.008

Owing to the increased accuracy of the positional coordinates obtained from the three-dimensional refinement it was decided to remeasure the unit-cell parameters to an accuracy commensurate with the other measurements. This was accomplished by the Main & Woolfson (1963) method. The new values and their standard deviations obtained are:

$$a = 9.724 \pm 0.015, \quad b = 6.440 \pm 0.002, \\ c = 14.175 \pm 0.007 \text{ \AA}.$$

The standard deviations of the bond lengths were

Table 1. *Final positional coordinates*

Atom	$x$	$y$	$z$
K	0.1061	-0.1690	0.2951
O(1)	-0.0128	0.3262	-0.1185
O(2)	0.1297	0.0889	-0.1712
O(3)	0.2897	0.1080	0.0081
O(4)	0.1599	0.1037	0.1373
C	0.0548	0.0603	-0.0127
C(1)	0.0594	0.1658	-0.1099
C(2)	0.1740	0.0911	0.0510
H	-0.210	0.400	-0.142

Table 2. *Final  $b_{ij}$  values*

Atom	$b_{11}$	$b_{22}$	$b_{33}$	$b_{23}$	$b_{31}$	$b_{12}$
K	0.00930	0.02507	0.00447	0.00031	-0.00359	0.00112
O(1)	0.01228	0.02427	0.00353	-0.00293	0.00133	-0.00623
O(2)	0.00699	0.03687	0.00324	-0.00044	0.00080	0.00032
O(3)	0.00922	0.03364	0.00395	-0.00059	-0.00114	0.00812
O(4)	0.01588	0.03998	0.00327	-0.00256	0.00024	0.01121
C	0.00770	0.02634	0.00327	-0.00029	0.00157	-0.00207
C(1)	0.00631	0.02355	0.00383	-0.00120	-0.00104	-0.00271
C(2)	0.00744	0.02631	0.00309	0.00220	0.00013	-0.00053

calculated from Ahmed & Cruickshank's (1953) formula. The error due to the errors in the cell parameters is small and was ignored. The extent of the data collected along the three axes being different, Darlow's formula (1960) was employed to calculate the standard deviations of the bond angles.

### Molecular dimensions

All the relevant bond lengths and bond angles (Tables 3 and 4) were calculated from the final atomic parameters listed in Table 1.

Table 3. *Interatomic distances and bond angles*

*Italic numerals represent the general equivalent position numbers for  $Pbca$  (space group No. 61) as given in International Tables for X-ray Crystallography (1952)*

Bond	Length (Å)	Contact	Length (Å)
C-C5	1.367 ± 0.026	K-K3	4.033 ± 0.004
C-C(1)	1.537 ± 0.013	K-K6	4.266 ± 0.004
C-C(2)	1.482 ± 0.020	K-O(1)5	2.848 ± 0.010
C(1)-O(1)	1.255 ± 0.011	K-O(1)7	2.776 ± 0.010
C(1)-O(2)	1.211 ± 0.013	K-O(2)4	2.663 ± 0.010
C(2)-O(3)	1.284 ± 0.016	K-O(2)5	2.934 ± 0.010
C(2)-O(4)	1.234 ± 0.012	K-O(2)7	2.755 ± 0.010
O(1)2...O(3)	2.514 ± 0.011	K-O(3)4	3.208 ± 0.010
		K-O(4)1	2.892 ± 0.010
		K-O(4)3	3.123 ± 0.010

Bond angle	Angle
C5-C-C(1)	120.6 ± 1.0°
C5-C-C(2)	121.7 ± 0.8
C(1)-C-C(2)	117.6 ± 1.1
O(1)-C(1)-O(2)	125.6 ± 1.0
O(3)-C(2)-O(4)	124.1 ± 1.2
C-C(1)-O(1)	115.8 ± 0.9
C-C(1)-O(2)	118.6 ± 0.9
C-C(2)-O(3)	114.1 ± 0.8
C-C(2)-O(4)	121.7 ± 0.8
C(1)2-O(1)2...O(3)	120.3 ± 0.7
C(2)-O(3)...O(1)2	112.9 ± 0.7

Table 4. *O(n)-K-O(m) angles*

*Italic numerals represent the general equivalent position numbers for  $Pbca$  (space group No. 61) as given in International Tables for X-ray Crystallography (1952)*

Oxygen, (n)-(m)	Angle	Oxygen, (n)-(m)	Angle
(1)5-(1)7	122.5 ± 0.8°	(2)4-(2)5	145.8 ± 0.8°
-(2)4	122.2	-(2)7	94.5
-(2)5	44.6	-(3)4	60.2
-(2)7	80.2	-(4)1	81.1
-(3)4	166.1	-(4)3	146.6
-(4)1	66.0	(2)5-(2)7	110.0
-(4)3	80.7	-(3)4	142.0
(1)7-(2)4	99.7	-(4)1	64.6
-(2)5	78.4	-(4)3	67.6
-(2)7	137.6	(2)7-(3)4	86.0
-(3)4	67.6	-(4)1	135.6
-(4)1	86.2	-(4)3	63.6
-(4)3	83.8	(3)4-(4)1	126.6
		-(4)3	91.7
		(4)1-(4)3	132.2

### General features

Like most other potassium salts of carboxylic acids, dipotassium ethylenetetracarboxylate is composed of alternate layers of cations and anions. The anions are so oriented that there are layers of oxygen atoms on either side of the layers of potassium ions. The potassium atoms are arranged in an approximately square array with K-K distances of 4.033 and 4.266 Å and K-K-K angles of 74.5, 106.0, 159.8 and 98.0°.

From an examination of the K-O distances in the structure it is apparent that each potassium atom is surrounded by eight oxygen atoms, 2 of type O(1), 3 of type O(2), 1 of type O(3) and 2 of type O(4), as shown in Figs. 3 and 4. That there is no other

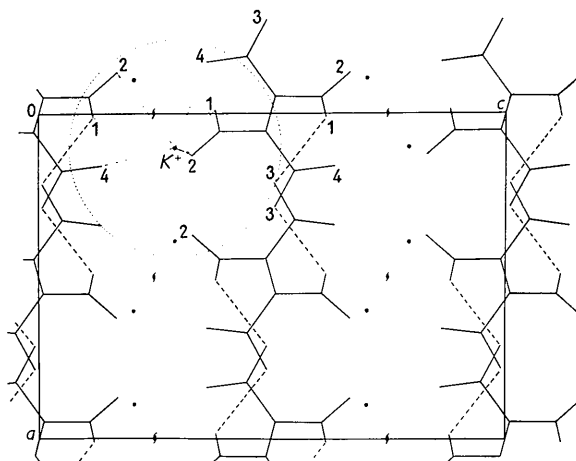


Fig. 3. The structure projected down the  $b$  axis. The dots represent  $K^+$  ions, and the circle round  $K^+$  has a radius of 3.2 Å. The numbers are those of the oxygen atoms, and the eight dotted K-O lines are those contacts listed in Table 3. The dashed lines represent the hydrogen bonds, of length  $2.514 \pm 0.011$  Å.

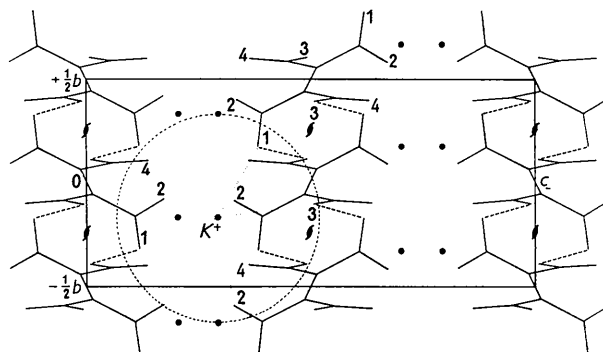


Fig. 4. The structure projected along the  $a$  axis. Symbols as in Fig. 3.

oxygen strongly linked with the potassium is shown by the absence of any K-O vector in the range 3.20-3.50 Å. The distances observed in some other

Table 5. K-O distances in potassium salts

Compound	Potassium coordination number	K-O distances	Reference
Potassium hydrogen bisphenylacetate	6	2.75, 2.88 Å	Speakman (1949)
Potassium dinitrosulphite	8	2.80-3.20	Cox, Jeffrey & Stadler (1949)
Potassium sulphamate	6 + 2N	2.75, 2.96	Brown & Cox (1940)
Potassium hydrogen di- <i>p</i> -hydroxy-benzoate hydrate	6	2.70, 3.10	Skinner & Speakman (1951)
Potassium benzyl penicillin	7	2.75-2.98	Beevers & Hughes (1941)
Potassium hydrogen maleate	8	2.817, 2.891, 2.873, 3.025	Darlow & Cochran (1961)

corresponding potassium compounds are given in Table 5. In each case the potassium atoms are sandwiched between layers of oxygen atoms.

### Planarity of the anion

The equation of the best plane passing through the six carbon atoms was found to be

$$-0.4662x + 0.8064y + 0.3881z = 0.$$

The deviations of all the atoms from this plane are given in Table 6. The standard deviation of the

Table 6. Deviations from the best plane through the six carbon atoms in dipotassium ethylenetetra-carboxylate

Atom	Displacement
C	0.006 Å
C(1)	-0.001
C(2)	-0.001
O(1)	1.098
O(2)	-1.043
O(3)	-0.652
O(4)	0.600
H	2.23
K	0.285

positional coordinates of the carbon atoms being of the order of 0.01 Å, their deviations from the best plane are not significant.

### Discussion of the structure

Table 6 shows that the oxygen atoms are not in the carbon plane, indicating that the strain in the anion if it were planar would be so great that the planarity of the hydrogen maleate anion could not be retained. The strain has been relieved by the rotation of the carboxylic groups about C-C bonds. The greater rotation of the group C(1)  $\begin{matrix} \text{O}(1) \\ \text{O}(2) \end{matrix}$  rather than C(2)  $\begin{matrix} \text{O}(3) \\ \text{O}(4) \end{matrix}$  is due to the former being more strongly linked with potassium.

The predicted configuration of the carboxylic group is that with the O-C-O angle equal to 125.5°. The observed values of O(1)-C(1)-O(2) = 125.6 ± 1.0° and

O(3)-C(2)-O(4) = 124.1 ± 1.2° compare very favourably with this.

The bond character of the C-O bonds was found by Pauling's (1950) method from the bond lengths and Hahn's method (1957) from the C-C-O bond angles. The results obtained are given in Table 7 as ranges of values corresponding to a 10% level of significance (± 2σ). The values obtained are consistent.

Table 7. Bond characters of the C-O bonds

Bond	Double bond character	
	Pauling's method	Hahn's method
C(1)-O(1)	38-63%	32-52%
C(1)-O(2)	63-100	50-70
C(2)-O(3)	20-45	13-33
C(2)-O(4)	50-87	61-81

The observed length of 1.367 ± 0.026 Å for the C=C double bond is longer than the value of 1.337 Å in ethylene obtained by Allen & Plyler (1958) but the difference (1.2σ) is not significant.

A recent estimate of the distance between trigonally linked carbon atoms by Dewar & Schmeising (1959) and Cruickshank & Sparks (1960) is 1.477 Å for the *sp*<sup>2</sup>-*sp*<sup>2</sup> single bond. The observed length of 1.482 ± 0.020 Å for the C-C(2) bond compares favourably with this, but the length of 1.537 ± 0.013 Å for the C-C(1) bond is significantly larger, the difference being 4.2σ. There seems to be no obvious explanation of this, although the tilt of the carboxyl groups out of the carbon plane slightly lengthens these bonds.

### Nature of the H-bond

It has not been possible to determine the position of hydrogen with certainty, or at least the present position produces neither a very significant drop in the residual (the inclusion of hydrogen decreases the residual by 0.2%) nor a pronounced improvement in the agreement of the observed and calculated structure factors for the low angle reflexions. This may be due to the incomplete nature of the absorption correction applied, as the irregular shape of the crystal made



the determination of the exact absorption correction difficult. The absorption factor varied from 0.16 for (002) to 0.51 for (020) amongst the inner reflexions, so that any error in it could mask the contribution of the hydrogen atom to the structure factors. Another cause could be the inaccuracies of the data arising from systematic errors in intensity measurement and scaling. The method of scaling the three-dimensional data necessitated frequent rescaling in the course of the refinement.

From an examination of all the O-O distances in the structure, however, it is clear that there is an intermolecular hydrogen bond, since the O(1)2-O(3) contact (Table 3) is  $2.514 \pm 0.011$  Å long, whilst the two next shortest O-O contacts for oxygen atoms not in the same carboxyl group are 2.98 and 3.11 Å. This intermolecular hydrogen bond means that because of the double nature of the anion the strain in the anion is so great that the ion is neither planar nor has an internal hydrogen bond.

We wish to express our gratitude to Prof. H. Lipson for his constant interest. All the computations were performed on the Mercury Computer of the Manchester University Computing Laboratory and we take great pleasure both in thanking Prof. F. C. Williams for extending this facility to us and in thanking those who have let us use their programs. One of us (S. K. K.) would also like to express thanks to the Principal and the Governing Body of the Hans Raj College, Delhi, India for the granting of study leave and to the British Council for providing the travel grant under the Commonwealth University Interchange Programme.

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## Scattering Factors Computed from Relativistic Dirac-Slater Wave Functions\*

BY DON T. CROMER AND J. T. WABER

*University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico, U.S.A.*

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Scattering factors for a total of 208 neutral atoms, positive ions and a few negative ions are given in tabular form and as nine-parameter analytic functions. These scattering factors have been computed from relativistic self-consistent field wave functions which include Slater's approximate exchange correction.

### Introduction

Two extensive tabulations of scattering factors have recently been published. Hanson, Herman, Lea &

\* Work performed under the auspices of the U.S. Atomic Energy Commission.

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Skillman (1964) have computed, for neutral elements from  $Z=1$  to  $Z=100$ , scattering factors based on self-consistent field Hartree-Fock-Slater (HFS) wave functions which had been computed by Herman & Skillman (1963). For these wave functions, Slater's (1951) approximate  $\rho^{\frac{1}{2}}$  method rather than Fock's