Table 4 (*cont.*)

Angles

Standard deviations are 0·5° in each case.

P(1)(1)–Cd–P(1)(2)	126·3°
P(1)(1)–Cd–P(2)(1)	95·6
P(1)(1)–Cd–P(2)(2)	105·4
P(1)(2)–Cd–P(2)(1)	115·9
P(1)(2)–Cd–P(2)(2)	110·5
P(2)(1)–Cd–P(2)(2)	99·2

Short P–P bonds

Bond lengths

Standard deviations are 0·018 Å in each case.

P(1)(1)–P(2)(1)	2·386 Å
P(1)(1)–P(2)(2)	2·050

Angles

Standard deviations are 0·7° in each case.

P(2)(1)–P(1)(1)–P(2)(2)	108·0°
P(1)(1)–P(2)(2)–P(1)(3)	105·7

For location of atoms see Fig. 2.

really a projection of the structure along [010], P atoms at the same position in the projection, but a distance *b* apart, are slightly displaced from each other to give the diagram a three-dimensional effect. The atoms in each chain are joined by broken lines and the diagram shows three rows of chains, the chains in each row being one above the other perpendicular to the plane of the projection. Such rows are joined together by one quarter of the tetrahedral bonds from Cd to P(1) in each case. The chains in each row are joined by the remaining tetrahedral bonds, two to P(2) atoms and one to a P(1) atom from each Cd.

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On the Additivity of Crystal Radii in Alkali Halides

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The additivity of crystal radii in alkali halides has been studied by applying the method of least squares to the experimental nearest-neighbour distances, d_{ah}. The result is a basic set of crystal radii, r_a and r_h ($r_{\mathrm{Li}}=1\cdot038$, $r_{\mathrm{Na}}=1\cdot295$, $r_{\mathrm{K}}=1\cdot617$, $r_{\mathrm{Rb}}=1\cdot759$, $r_{\mathrm{C}}=2\cdot017$, $r_{\mathrm{F}}=1\cdot019$, $r_{\mathrm{Cl}}=1\cdot534$, $r_{\mathrm{Br}}=1\cdot695$, $r_{\mathrm{I}}=1\cdot934$ Å), and an additive correction c (r_a+c, r_h-c). Theoretically the constant c has the value zero. The best agreement of the least-square radii with the experimental radii was achieved with the value $c_{\mathrm{exp}}=(-0\cdot114\pm0\cdot014)$ Å. The cation radii decreased and anion radii increased in comparison with the basic values ($c=0$) resulting from the ionic character of alkali halides. The root-mean-square deviation of the radii sum, r_a+r_h, from the experimental d_{ah} values is 0·021 Å, and the r.m.s. deviation of the values r_a+c_{exp}, r_h-c_{exp} from the experimental radii, 0·058 Å.

Crystal radius

Disregarding the small non-sphericity of atoms in a crystal lattice and taking into account the low compressibility of crystalline solids, a crystal can be approximated to a solid composed of hard atomic spheres. Strictly, of course, those spheres are neither hard nor spherical, as can be seen quite clearly from electron density maps (see *e.g.* Witte & Wölfel, 1955). Therefore, the radius of an atom in a crystal – crystal radius – does not have any accurate meaning and can have various definitions.

The classical way to determine the crystal radii in a family of salts, as in the alkali halides, is to fix the radius ratios of the alkali and halogen ions in one crystal by use of a suitable physical criterion. Well known examples are the radii evaluated by Wasastjerna (1923), Goldschmidt (1926), Pauling (1927) and Zachariasen (1931).

Fumi & Tosi (1964) have reported a set of crystal radii based on the Pauling and Huggins–Mayer forms (Fumi & Tosi, 1964), and on the Born–Mayer form (Tosi & Fumi, 1964) of the repulsive energy (see also Tosi, 1964). The procedure is cumbersome, but yields values in fairly good agreement with the experimental ones derived from the X-ray measurements of electron distributions in crystals (Inkinen & Järvinen, 1968; Järvinen & Inkinen, 1967; Krug, Witte & Wölfel, 1955; Kurki-Suonio & Fontell, 1964; Meisalo & Inkinen, 1967; Merisalo & Inkinen, 1966; Schoknecht, 1957; Witte & Wölfel, 1955; see Table 2).

A report concerning ionic radii in alkali halides has also been given by Maslen (1967). He compares Pauling radii and Fumi & Tosi values, and also gives radii in nine crystals, based on the criterion of minimum electron density or minimum overlap in the theoretical crystal-lattice superposition.

A very different set of radii – atomic radii – has been introduced, and tested in over 1200 cases of internuclear distances with an average deviation of about 0·12 Å, by Slater (1964). By use of Bragg's simple principle of touching atomic spheres (Bragg, 1920) Slater starts numerically from elements forming compounds with tetrahedral coordination. He reports atomic radii of 86 elements; most values are clearly correlated with, and in many cases practically equal to, the radii of the theoretical radial charge density maxima of the outermost electron shells (Slater, 1965, p. 103).

Most discussions concerning crystal radii, in alkali halides especially, are based on the obvious additivity of those radii. The usual statement is that one only needs to fix one radius or the radii ratio in one crystal in order to get the whole set. Further, with complicated refinements of the theory the radii become individual-crystal-dependent (Tosi, 1964; Maslen, 1967). However, as Slater states, 'with all this elaboration, the simple fact has rather been lost in sight, that by the straightforward use of a single set of radii, one can do fairly well' (Slater, 1965, p. 97). Such a single set of radii, as precisely additive as possible, can be achieved trivially by applying the well-known method of least squares to the experimental nearest-neighbour distances.

The method of least squares

Additivity of crystal radii means qualitatively that various interionic distances can be reproduced with satisfactory precision on the basis of a single set of radii. Quantitatively this precision can be expressed in terms of the root-mean-square deviation. In the alkali halide family, the best fit to the experimental nearest-neighbour distances, d_{ah}, (Hietala, 1963; *Nat. Bur. Stand. Circ.* 1953–57; Pautamo, 1963) is achieved with the alkali and halide radii, r_a and r_h, which satisfy the condition

$$S=\Sigma_{ah}(r_a+r_h-d_{ah})^2=\text{minimum}; \qquad (1)$$

the summation is from 1 to $n_a=5$ for alkali ions and from 1 to $n_h=4$ for halide ions.

We begin with the values

$$r_a^{(1)}=(1/2n_h)\Sigma_h d_{ah} \text{ and } r_h^{(1)}=(1/2n_a)\Sigma_a d_{ah} \qquad (2)$$

and continue the series as follows:

$$\begin{aligned} r_a^{(n)}&=r_a^{(n-1)}-(1/n_h)\Sigma_h(r_a^{(n-1)}+r_h^{(n-1)}-d_{ah})\,,\\ r_h^{(n)}&=r_h^{(n-1)}-(1/n_a)\Sigma_a(r_a^{(n-1)}+r_h^{(n-1)}-d_{ah})\,. \qquad (3)\end{aligned}$$

The sequence (2)→(3)→(3) yields $r_a^{(n)}=r_a^{(n-1)}$ and $r_h^{(n)}=r_h^{(n-1)}$ with $n=3$, *i.e.* the series have terminated in constant values,

$$\begin{aligned} r_a=r_a^{(2)}&=(1/n_h)\Sigma_h d_{ah}-(1/2n_a n_h)\Sigma_{ah}d_{ah}\,,\\ r_h=r_h^{(2)}&=(1/n_a)\Sigma_a d_{ah}-(1/2n_a n_h)\Sigma_{ah}d_{ah}\,, \qquad (4)\end{aligned}$$

depending only upon the primary d_{ah} values.

In order to see if the radii in equations (4) satisfy the least-squares condition (1), we add arbitrary constants, c_a and c_h, to r_a and r_h respectively, and insert these

Table 1. *The basic (equal to the theoretical) least-square radii, r_a and r_h, experimental nearest-neighbour distances, d_{ah}, and deviations $\Delta_{ah}=r_a+r_h-d_{ah}$ and Δ_{ah}/d_{ah}*

		F	Cl	Br	I
		1·019	1·534	1·695	1·934
Li	1·038	2·014	2·570	2·751	3·000
		0·043	0·002	−0·018	−0·028
		2·14%	0·08%	−0·65%	−0·93%
Na	1·295	2·317	2·820	2·989	3·237
		−0·003	0·009	0·001	−0·008
		−0·13%	0·32%	0·03%	−0·25%
K	1·617	2·673	3·147	3·298	3·533
		−0·037	0·004	0·014	0·018
		−1·38%	0·13%	0·42%	0·51%
Rb	1·759	2·815	3·290	3·444	3·671
		−0·037	0·003	0·010	0·022
		−1·31%	0·09%	0·29%	0·60%
Cs	2·017	3·004	3·571	3·720	3·956
		0·032	−0·020	−0·008	−0·005
		1·07%	−0·56%	−0·22%	−0·13%
r.m.s. deviation		0·021			
|%| deviation		0·56%			

'corrected' values into the square sum (1). With the aid of the expressions (4) we get

$$S' = \Sigma_{ah}(r_a + r_h - d_{ah})^2 + \Sigma_{ah}(c_a + c_h)^2, \qquad (5)$$

which is seen to have its minimum value if, for all pairs a and h, $c_a + c_h = 0$, *i.e.*

$$c_a = -c_h = c = \text{arbitrary constant}\,. \qquad (6)$$

Thus, the basic radii (4) satisfy the condition (1) and every least-square set of alkali and halide radii can be derived from them by use of a suitable additive constant, c:

$$r'_a = r_a + c \quad \text{and} \quad r'_h = r_h - c\,. \qquad (7)$$

Additional conditions

The volume available for an ion in the crystal lattice is limited and can be approximated by a box (Sysiö, 1962, 1967); the smaller the ion itself the greater its excess space and the lower its box-energy (kinetic energy). The coulombic (potential) energy is constant because the nearest-neighbour distances, d_{ah}, are fixed. Thus, in order to satisfy the minimum-energy condition the box-energy must also have a minimum value. This means, roughly, having radii $r_a + c$ and $r_h - c$ as small as possible, which can be expressed quantitatively as follows:

$$S'' = \Sigma_{ah}[(r_a + c)^2 + (r_h - c)^2] = \text{minimum}\,. \qquad (8)$$

By taking (4) into account (8) can be reduced to

$$S'' = \Sigma_{ah}(r_a^2 + r_h^2) + 2n_a n_h c^2, \qquad (9)$$

which will have a minimum value when

$$c = 0\,. \qquad (10)$$

If the expressions (4) are inserted into the square sum of radii differences, $\Sigma_{ah}(r_a - r_h + 2c)^2$, this is also seen to have a minimum value because of the condition (10). Thus, within the alkali halide family and within the condition (1) the anion radius is as nearly equal as possible to the cation radius.

From the experimental point of view, the best radii (7) would be as close as possible to the experimental values (Table 2). This requirement can be expressed quantitatively as follows

$$S''' = \Sigma_{ah}[(r_a + c - r_{a\,\mathrm{exp}})^2 + (r_h - c - r_{h\,\mathrm{exp}})^2] = \text{minimum}, \qquad (11)$$

where the summation includes all the pairs of experimental alkali and halide radii, $r_{a\,\mathrm{exp}}$ and $r_{h\,\mathrm{exp}}$, n_{ah} in number. The possible turning points of the sum $S''' = S'''(c)$ are defined by the equation $dS'''/dc = 0$, which has the single root

$$c_{\mathrm{exp}} = -(1/2n_{ah})\Sigma_{ah}(r_a - r_{a\,\mathrm{exp}} - r_h + r_{h\,\mathrm{exp}})\,. \qquad (12)$$

The second derivative has the positive value $d^2S'''/dc^2 = 4$, *i.e.* $S''' = S'''(c_{\mathrm{exp}})$ is a minimum point.

Numerical

The expressions (4) give a single set of crystal radii once the nearest-neighbour distances, d_{ah}, of the whole

Table 2. *Various sets of alkali and halide radii and mean deviations of their sums from the experimental nearest-neighbour distance and experimental radii and their accuracy limits*

	Li	Na	K	Rb	Cs	F	Cl	Br	I	Δ	r.m.s.	|%|
Wasastjerna (1923)	–	1·01	1·30	1·50	1·75	1·33	1·72	1·92	2·19	−0·038	0·063	1·72
Goldschmidt (1926)	0·78	0·98	1·33	1·49	1·65	1·33	1·81	1·96	2·20	−0·020	0·052	1·16
Pauling (1927)*	0·60	0·95	1·33	1·48	1·69	1·36	1·81	1·95	2·16	−0·057	0·097	2·34
Zachariasen (1931)*	0·68	0·98	1·33	1·48	1·67	1·33	1·81	1·96	2·19	−0·031	0·051	1·09
Fumi & Tosi (1964)* Basic H–M	0·914	1·254	1·539	1·667	1·804	1·199	1·608	1·736	1·924	−0·012	0·074	2·11
Mean H–M	0·94	1·24	1·54	1·68	1·83	1·16	1·62	1·76	1·97	0·003	0·042	1·19
Tosi & Fumi (1964)* Basic B–M	0·816	1·170	1·463	1·587	1·720	1·179	1·585	1·716	1·907	−0·117	0·138	3·94
Mean B–M	0·90	1·21	1·51	1·65	1·80	1·19	1·65	1·80	2·01	0·006	0·041	1·17
Maslen (1967) Minimum overlap	0·70	0·98	1·34	–	–	1·35	1·81	1·98	–	−0·011	0·037	1·19
Minimum density	0·85	1·12	1·45	–	–	1·26	1·67	1·81	–	−0·011	0·060	2·13
Slater (1964) Atomic radii	1·45	1·80	2·20	2·35	2·60	0·50	1·00	1·15	1·40	0·002	0·073	2·06
Present work Basic set	1·038	1·295	1·617	1·759	2·017	1·019	1·534	1·695	1·934	0·000	0·021	0·56
Inkinen & Järvinen (1968)	0·91						1·66			±0·08		
Järvinen & Inkinen (1967)				1·71			1·58			±0·05		
Krug, Witte & Wölfel (1955)	0·92					1·09				±0·1†		
Kurki-Suonio & Fontell (1964)		1·15					1·67			±0·06		
Meisalo & Inkinen (1967)			1·57					1·73		±0·07		
Merisalo & Inkinen (1966)	0·78					1·23				±0·04		
Schoknecht (1957)		1·18					1·64			±0·1†		
Witte & Wölfel (1955)		1·17					1·65			±0·1†		
Gourary & Adrian (1960)‡	0·94	1·17	1·49	1·63	1·86	1·16	1·64	1·80	2·05	–	0·028	0·66
Present work $c_{\mathrm{exp}} = -0{\cdot}114$	0·924	1·181	1·503	1·645	1·903	1·133	1·648	1·809	2·048	±0·014	0·021	0·56

* For NaCl-type crystals only.

† According to Schoknecht.

‡ Nor for LiF, based on the values of Witte *et al.*

crystal family are known. In fact, the iteration process (2)→(3) would yield a set of radii although some d_{ah} values were unknown. Starting values d_{ah} (Hietala, 1963; *REP. Nat. Bur. Stand.* Circ. 1953–57; Pautamo, 1963) and the resulting basic (theoretical) radii, r_a and r_h, together with the deviations $\Delta_{ah}=r_a+r_h-d_{ah}$ and Δ_{ah}/d_{ah} (per cent) are presented in Table 1.

In order to make comparisons easier, all the theoretical sets and experimental pairs of radii mentioned in the introduction, as well as the basic (theoretical) least-square values (4) and corresponding semi-experimental radii defined by the equations (4), (7) and (12) are collected in Table 2. On the basis of the 16 experimental radii (8 pairs) given in Table 2 and by taking into account the root-mean-square value of their accuracy 0·055 Å, the correction (12) to the basic radii (4) has the value $c_{\text{exp}}=(-0{\cdot}114\pm0{\cdot}014)$ Å. The main reason for this radii shift, *i.e.* charge shift also, is the ionic character of the alkali halide crystals.

As seen in Table 1, the least-square radii reproduce most interionic distances very well. The greatest deviation, $(r_a+r_h-d_{ah})/d_{ah}=2{\cdot}14\%$, found in LIF is probably caused by the strong ionic attraction. If the r.m.s. deviation of the radii sum from the experimental nearest-neighbour distance is chosen as a criterion for the additivity of crystal radii, the least-square sets are clearly the best (Table 2).

Another possible basis for comparison is the agreement of a set of radii with the experimental values. These root-mean-square deviations, D, and the corresponding corrections, c_{exp}, (7), (12), which would minimize D, are shown in Table 3. According to the D values the mean Born–Mayer set of Tosi & Fumi is the 'best' ($D=0{\cdot}056$ Å), the semi-experimental least-square radii are the second best (0·058 Å) and the Gourary–Adrian values the third best (0·061 Å). The basic (theoretical) least-square set comes eight – before the classical values of Wasastjerna, Goldschmidt, Pauling and Zachariasen, and before the atomic radii of Slater.

Table 3. *The root-mean-square deviation, D, of various sets of radii from the experimental radii, and the additive correction,* c_{exp} $(r_a+c_{\text{exp}},\ r_h-c_{\text{exp}})$, *which would minimize D*

		D	c_{exp}
Wasastjerna (1923)		0·160	0·145
Goldschmidt (1926)		0·180	0·169
Pauling (1927)		0·219	0·212
Zachariasen (1931)		0·195	0·189
Fumi & Tosi (1964)	Basic H–M	0·065	−0·025
	Mean H–M	0·063	−0·028
Tosi & Fumi (1964)	Basic B–M	0·070	0·008
	Mean B–M	0·056	0·005
Maslen (1967)	Minimum overlap	0·192	0·185
	Minimum density	0·073	0·050
Slater (1964)	Atomic radii	0·628	−0·626
Present work	Basic set	0·128	−0·114
	'exp' set	0·058	0·000
Gourary & Adrian (1960) 'exp'		0·061	0·001

Summary

Application of the well-known method of least squares to the experimental nearest-neighbour distances, d_{ah}, has yielded a basic set of crystal radii, r_a and r_h, and an unlimited number of other sets which can be derived from the basic values with an arbitrary constant c as follows: $r'_a=r_a+c$, $r_h=r'_h-c$. The sum of those radii r_a+r_h, reproduces most interionic distances, d_{ah}, very well; the overall root-mean-square deviation is 0·021 Å. Thus, additivity of the least-square radii is good – in fact best in comparison with other sets of radii.

A theoretical value for the constant c has been deduced from the minimum-energy condition. According to the result $c=0$ the basic and theoretical least-square radii are equal. They agree with the 'best' theoretical sets (Fumi & Tosi, 1964; Tosi & Fumi, 1964) and also satisfactorily with the experimental radii – better than the classical values of Wasastjerna, Goldschmidt, Pauling and Zachariasen.

By fitting the least-square radii, r_a+c and r_h-c, as closely as possible to the experimental radii the constant c takes the value $c_{\text{exp}}=(-0{\cdot}114\pm0{\cdot}014)$ Å. The cation radii are decreased and anion radii increased in comparison with the basic values ($c=0$) because of the ionic character of alkali halides. This semi-experimental least-square set is based on sixteen experimental radii and agrees with them well, the root-mean-square deviation (0·058 Å) being only a little greater than the r.m.s. accuracy of the experimental radii (0·055 Å).

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Crystal and Molecular Structure of α,α,′α,α′-Tetramethyl-β-ketoglutaric Acid (Triclinic Modification). A Model of Polydimethylketene with Ketonic Enchainment

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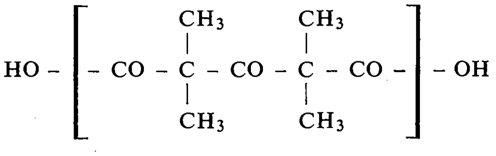
The crystal and molecular structure of the title compound has been determined. The space group is $P\bar{1}$, with unit-cell parameters: $a=7{\cdot}07\pm0{\cdot}01$, $b=6{\cdot}13\pm0{\cdot}01$, $c=13{\cdot}13\pm0{\cdot}02$ Å; $\alpha=81°23'\pm30'$, $\beta=96°42'\pm30'$, $\gamma=118°23'\pm30'$. Three-dimensional X-ray diffraction data were collected by photographic methods. Signs of structure factors were determined by the direct methods of Sayre, Cochran and Zachariasen (*Acta Cryst.* (1952), 65, 68). Refinement was carried out by least-squares methods. The values of the rotation angles around the C–C bonds adjacent to the central carbonylic group are 66° and −155° ($G+,T$ type). Some valence angles on carbon atoms are larger than the expected normal values because of strong intramolecular interactions. The molecular conformation is similar to that found for the chain of ketonic polydimethylketene.

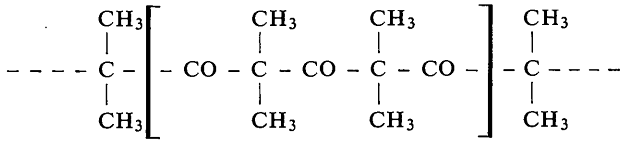
Introduction

This paper describes the structural analysis of α,α,α′,α′-tetramethyl-β-ketoglutaric acid (TMKGA),



$$\mathrm{HO}-\left[-\mathrm{CO}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{CO}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{CO}-\right]-\mathrm{OH}$$

The part of the molecule in brackets is a fragment of the chain of polydimethylketene,



$$----\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}-\left[-\mathrm{CO}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{CO}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{CO}-\right]-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}----$$

a polymer whose crystal structure has been recently studied in our laboratory (Bassi, Ganis & Temussi, 1967).

The molecular structure of polydimethylketene is characterized by very short intramolecular distances, *e.g.* $\mathrm{CH_3}$---$\mathrm{CH_3}$ distances of the order of 3 Å and O---O distances of the order of 2·8 Å, which are certainly surprising, even considering the limited accuracy inherent in fibre spectra crystal structure analyses.

Our interest in the X-ray study of TMKGA originated in part from the possibility of finding similar intramolecular distances in a model compound. From a more general point of view it was our purpose to gain new data on some conformational parameters (bond lengths, valence angles, torsional angles) in overcrowded open-chain aliphatic molecules, since very few values are available in the literature. In this connexion it is worth mentioning that the choice of such conformational parameters in order to build preliminary molecular models for the structural analysis, and for the calculation of the internal conformational energy of polydimethylketene (Ganis & Temussi, 1966) has been particularly difficult owing to the lack of reliable values for valence angles of the type present in TMKGA