Crystal Structures of the Acid Salts of Some Dibasic Acids. Part VI.[1] An *X*-Ray Study of Potassium Hydrogen Glutarate

By **A. L. Macdonald** and **J. C. Speakman,*** Chemistry Department, The University, Glasgow G12 8QQ, Scotland

The title compound crystallises with $Z = 4$ in a cell with $a = 18{\cdot}476(4)$, $b = 7{\cdot}282(3)$, $c = 5{\cdot}133(1)$ Å, space group *Cmma*. The structure has been refined to R 3·35% for 627 independent, non-zero reflexions obtained from diffractometer measurements. It embodies infinite chains of glutarate residues (of *mm* symmetry) linked end-to-end by hydrogen bonds across points of 2/*m* symmetry. The hydrogen bonds are very short, with $O \cdots H \cdots O$ 2·445(3) Å. The vibrational movements of the glutarate residue are analysed. The librational component is large in the one direction where it is unconstrained by the hydrogen bonding, and negligibly small in the other two directions.

CONTINUING our studies[2] of the acid salts formed by the simple, symmetrical dicarboxylic acids, we have now examined salts of glutaric acid, $HO_2C{\cdot}[CH_2]_3{\cdot}CO_2H$ (H_2G). For the salt of an organic acid, $RbHG$ has a crystal structure of remarkably high symmetry.[3] With the object of curtailing absorption errors, so as to make a more accurate study of this structure, we prepared the corresponding ammonium salt. Though the unit-cell dimensions of NH_4HG and $RbHG$ are almost identical (see later), and their crystal habits generally the same, these acid salts actually belong to different space groups; an account of their structural relationship has been published.[3] The (usually) different crystal habit of KHG conceals its close isomorphism with $RbHG$. When we had penetrated this disguise, we collected full *X*-ray data on the potassium salt. We now report the results of the subsequent analysis. Some neutron-diffraction measurements have also been made.[4]

Description of the Structure.—The crystal data (see later) imply the following molecular symmetry: the potassium ion is at a site of symmetry 222; the acidic hydrogen atom at one of symmetry 2/*m*; the glutarate residue has *mm* symmetry. This neat arrangement of the atoms is shown, together with the numbering system, in the Figure. All the atoms, except H(2), are in special positions. No more than fourteen positional parameters suffice to define the crystal structure of $KH(C_5H_6O_4)$. Bond-lengths and angles within, and between, the HG^- residues are listed in Table 1.

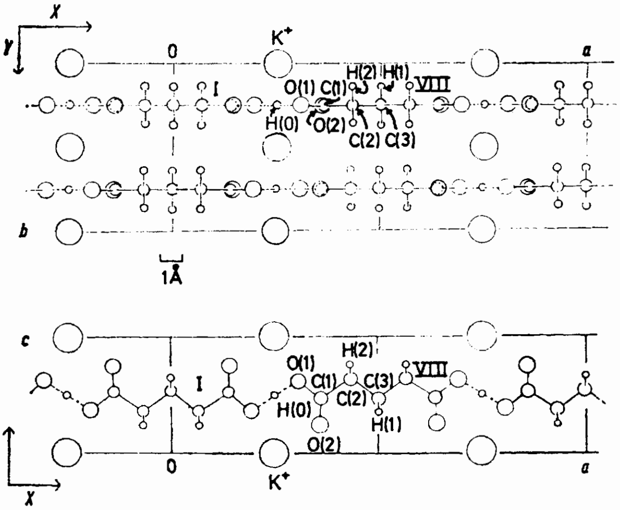

FIGURE The crystal structure of potassium hydrogen glutarate, seen in its *c* and *b* axial projections. In the lower picture, only the glutarate chain at *b*/4 is shown. The CCU consists of the half-molecule whose atoms are numbered

The interest of this structure lies in the organisation of the acid-anions to yield an elegant example of a

---

[1] Part V, A. McAdam and J. C. Speakman, *J. Chem. Soc.* (*A*), 1971, 1997.

[2] Part II, J. G. Sime, J. C. Speakman, and R. Parthasarathy, *J. Chem. Soc.* (*A*), 1970, 1919, and later papers.

[3] A. L. Macdonald and J. C. Speakman, *J. Cryst. Mol. Structure*, 1971, **1**, 189.

[4] A. L. Macdonald, Ph.D. Thesis, University of Glasgow, 1971; to be submitted to *J.C.S.*

Type A_2 structure[5] (see Part II[2]). Symmetrical HG^- anions are linked into infinite chains, parallel to *a*, by symmetrical O $\cdots$ H $\cdots$ O bonds between the terminal carboxy-groups of neighbouring anions. The hydrogen bond is very short, and, in accordance with this, the i.r. spectrum is of Hadži's Type (ii).[6]

TABLE 1

Some bond-lengths (Å) and angles (degrees) involving the hydrogen-glutarate anion with standard deviations in parentheses

(*a*) Distances

C(1)–O(1)	1·299(2) [1·308] *	C(1)–C(2)	1·508(2) [1·516]
C(1)–O(2)	1·223(2) [1·247]	C(2)–C(3)	1·522(2) [1·530]
O(1) $\cdots$ O(1^{I})	2·445(3) [2·462]	C(2)–H(2)	0·96(3)
		C(3)–H(1)	0·97(4)

(*b*) Angles

C(2)–C(1)–O(1)	114·3(2)	H(2)–C(2)–H(2^{IX})	102(2)
C(2)–C(1)–O(2)	123·3(2)	C(1)–C(2)–H(2)	108(1)
O(1)–C(1)–O(2)	122·4(2)	H(1)–C(3)–H(1^{IX})	99(1)
		C(2)–C(3)–H(1)	112(1)
C(1)–O(1) $\cdots$ O(1^{I})	110·2(1)	C(3)–C(2)–H(2)	112(2)
C(1)–C(2)–C(3)	114·9(2)		
C(2)–C(3)–C(2^{VIII})	110·6(2)		

* The values in square brackets are corrected for libration.

Superior Roman numerals refer to the following equivalent positions relative to the CCU at *x*, *y*, *z*:

I	$\frac{1}{2} - x, y, -z$	VI	$x, -y, 1 - z$
II	$x, -y, -z$	VII	$x, y, -1 + z$
III	$\frac{1}{2} - x, -y, z$	VIII	$1 - x, y, z$
IV	$\frac{1}{2} - x, -y, -1 + z$	IX	$x, \frac{1}{2} - y, z$
V	$\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$		

Table 2 lists some details of the hydrogen bonding in the Type A_2 crystals which have been carefully studied. The bonds shown in this Table, together with those in a number of Type *A* acid salts of monocarboxylic acids,[7] constitute a remarkable set. They all lie across some element of two-fold crystallographic symmetry, and all are very short: weighted each according to its estimated precision, their mean is O $\cdots$ O 2·4467(11) Å. (The value in parentheses is a measure of the formal precision of the average. Of course, it does not represent true accuracy; nor is it likely that the real lengths of the hydrogen bonds in a score of different acid salts are the same.)

TABLE 2

The hydrogen bonds in some Type A_2 acid salts (MH*Y*) determined from *X*-ray analyses except where stated otherwise

H_2Y	M	Symmetry of bond	O $\cdots$ H $\cdots$ O (Å)	C–O $\cdots$ O (degrees)
Malonic	K	$\bar{1}$	2·459(5)	111·7[a]
			2·468(5)	111·6[b]
Succinic	K	2	2·446(4)	114·3[c]
			2·444(10)	115·3[d]
Glutaric	Rb	2/*m*	2·40(2)	113[e]
	NH_4	2	2·460(6)	113·5[e]
	K	2/*m*	2·445(3)	110·2[f]
Oxalic	N_2H_5	$\bar{1}$	2·450(4)	114·5[g]
			2·448(7)	114·5[h]

[Weighted mean 2·451(2).]

[a] Ref. 2. [b] Ref. 22; neutron diffraction. [c] Ref. 5. [d] Ref. 5; neutron diffraction. [e] Ref. 3. [f] This work. [g] N. A. K. Ahmed, R. Liminga, and I. Olovsson, *Acta Chem. Scand.*, 1968, **22**, 88. [h] A. Nilsson, R. Liminga, and I. Olovsson, *Acta Chem. Scand.*, 1968, **22**, 719; neutron diffraction.

There is a difficulty in deciding, from diffraction methods, whether the effective symmetry of such hydrogen bonds owes anything to disorder.[8] From other considerations, which have been fully discussed in parallel cases,[8-12] we think it probable that the O $\cdots$ H $\cdots$ O bond in KH*G* has its proton vibrating anharmonically in a broad, single, potential-energy well.

Analysis of the Vibration of the Glutarate Residue.—That intermolecular hydrogen bonding tends to restrict molecular vibration has been recognised for many years. Amongst simple organic crystals, for example, hydrogen-bonded structures can often be diagnosed merely by inspection of *X*-ray photographs. The fall-off of intensity of the reflexions with Bragg angle is usually less rapid than it is for a structure without intermolecular hydrogen bonds. Examples have been given by Robertson,[13] who also pointed out that the effect is not uniform. Curtailment of vibration may be evident only in certain directions.

An elementary exposition is as follows. Simple molecules that are non-polar generally pack together very efficiently,[14] so that van der Waals contacts are made at many points between a given molecule and its neighbours. As the environment is therefore uniform, and as the van der Waals attraction is weak, moderate vibration can occur in all directions. *X*-Ray intensities are thereby weakened, and, because of the librational components of the molecular vibration in particular, they fall off sharply with Bragg angle. When the molecules have peripheral groups which can form intermolecular hydrogen bonds, this possibility takes precedence in organising the packing. It usually leads to a more open style of structure, with fewer points of contact, but at these points the forces of attraction are stronger. Consequently molecular vibration, and libration in particular, may become more vigorous, but only in directions where the movement can occur without unduly stretching the hydrogen bonds. Librations of a character likely to change the O–H $\cdots$ O distances will be severely curtailed. This differentiation is particularly marked where the hydrogen bonds are strong.

These principles find support in a number of structural studies where the precision achieved has been good

---

[5] A. McAdam, M. Currie, and J. C. Speakman, *J. Chem. Soc.* (*A*), 1971, 1994; see also ref. 22.

[6] D. Hadži, *Pure Appl. Chem.*, 1965, **11**, 435.

[7] J. C. Speakman, *Chem. Comm.*, 1967, 32.

[8] B. L. McGaw and J. A. Ibers, *J. Chem. Phys.*, 1963, **39**, 2677.

[9] R. H. Ellison and H. A. Levy, *Acta Cryst.*, 1965, **19**, 260.

[10] A. Sequeira, C. A. Berkebile, and W. C. Hamilton, *J. Mol. Structure*, 1967—8, **1**, 283.

[11] A. L. Macdonald, J. C. Speakman, and D. Hadzi, *J.C.S. Perkin II*, 1972, 825.

[12] J. C. Speakman, *Structure and Bonding*, 1972, **12**, in the press.

[13] J. M. Robertson, *Z. Krist.*, 1959, **112**, 68; see also J. L. Amorós and M. L. Canut, *Bol. esp. Hist. nat. G*, 1958, **56**, 25.

[14] A. I. Kitaigorodskii, 'Organic Crystal Chemistry,' Consultants Bureau, New York, 1961.

enough to warrant a detailed vibrational analysis: for instance, in β-succinic acid,[15] ammonium oxamate,[16] the two forms of oxalic acid dihydrate,[17] and α-resorcinol.[18] The succinic acid molecule, for example, librates with a root mean-square amplitude of 9° about an axis parallel to its greatest length, whilst torsional oscillation in other directions is insignificant. In contrast, the amplitudes of the naphthalene molecule about its three principal axes are all between 2 and 4°.[19]

Because of the high symmetry of the anion in KH*G*, and because all the atoms have small (indeed, negligible) values for the single cross-term, U_{31}, consideration of its molecular vibration can follow the simple lines suggested by Beagley and Small.[16] The individual atomic vibrational parameters (see later) can be adequately interpreted in terms of a rigid molecule with root-mean-square translational amplitudes of 0·14, 0·21, and 0·18 Å in the direction of the x, y, and z axes, and with appreciable libration, of root-mean-square amplitude 12°, only about the axis of minimum inertia parallel to x. The only atomic parameters to deviate significantly from the requirements of this model are U_{11} for O(2) and U_{22} for C(2), which are, respectively, *ca.* 0·01 Å^2 too large and too small.

The part of the motion of O(1) which is due to libration takes place normal to the direction of the very strong O · · · H · · · O bond. Were there libration about the other two axes, parallel to z and y, it would impose increasing stresses on the hydrogen bond. Hydrogen bonding is, surely, a factor restricting torsional motion to the one direction.

Large torsional oscillation requires corrections to be made to molecular dimensions.[19] Values so amended are included in Table 1. We are inclined to give more weight to the uncorrected dimensions however, and for the following reasons. In Type *A* acid salts of monobasic acids the inhomogeneity of the molecular environment shifts the centre of oscillation away from the centre of mass towards the carboxy-group. Corrections in the neighbourhood of the hydrogen bond are therefore small and difficult to assess. Furthermore, application of rigid-body corrections, though it increases intramolecular distances, usually diminishes intermolecular (O · · · H · · · O) bond-lengths. (Exceptionally, it has the reverse effect in KH*G*.) As our work on Type *A* crystals has had, as one of its objectives, the search for very short hydrogen bonds, we have deemed it prudent to omit an uncertain correction which normally shortens the bond.* The values cited in Table 2 are uncorrected, as is the overall average given earlier.

One other aspect of the vibrational analysis must be discussed. Space-group symmetry requires the carbon and oxygen atoms of the glutarate residue to have their 'rest' positions identically on the plane $x,\frac{1}{4},z$. But the vibrational parameters of these atoms in the y direction (U_{22}) are all much greater than those along x or z. We then recall the debasement of symmetry and change of structure, when the potassium (or rubidium) atom was replaced by ammonium. This change, which was attributed[3] to the formation of N–H · · · O bonds, involved shifts of O(1) and O(2) in opposite directions out of the plane at $y = \frac{1}{4}$, and consequent smaller shifts of the carbon atoms. Does the higher symmetry in KH*G* depend on disorder? Is distortion of the individual glutarate unit concealed by a random arrangement of oppositely twisted units? In our discussion of the isomorphous RbH*G* we gave reasons for rejecting this notion. The vibrational analysis now given for KH*G* seems to account for our observed parameters adequately, without introducing hypothetical disorder.

TABLE 3

Comparison of dimensions of the anions in KH*Y* (distances in Å, angles in degrees)

H_2Y	Malonic	Succinic	Glutaric
C(3)–C(2)		1·510(5)	1·522(2)
C(2)–C(1)	1·516(4)	1·512(3)	1·508(2)
C(1)–O(1)	1·293(4)	1·301(2)	1·299(2)
C(1)–O(2)	1·223(4)	1·225(4)	1·223(2)
Σ	2·516	2·526	2·522
Δ	0·070	0·076	0·076
C(2)–C(3)–C(2)			110·6(2)
C(1)–C(2)–C(3)	119·4(4)	114·3(2)	114·9(2)
O–C–OH	123·1(3)	123·5(2)	122·4(2)
C–C–OH	112·5(3)	113·6(3)	114·3(2)
C–C–O	124·4(2)	122·9(2)	123·3(2)
Δ	11·9	9·3	9·0

TABLE 4

Environment of the potassium ion, which lies on a two-fold axis

(i) Distances (Å: standard deviations in parentheses)

$K^+ \cdots O(1)$	2·799(1)	$K^+ \cdots O(2)$	3·000(1)

(ii) Angles at K^+ (deg., standard deviations all *ca.* 0·04°)

$O(1^{IV}) \cdots O(1^{V})$	137·85	$O(1^{IV}) \cdots O(2^{II})$	63·80
$O(1^{IV}) \cdots O(1^{VI})$	98·87	$O(1^{IV}) \cdots O(2^{III})$	69·64
$O(1^{IV}) \cdots O(1^{VII})$	96·00	$O(2) \cdots O(2^{I})$	105·27
$O(1^{IV}) \cdots O(2)$	157·29	$O(2) \cdots O(2^{II})$	96·04
$O(1^{IV}) \cdots O(2^{I})$	83·35	$O(2) \cdots O(2^{III})$	129·15

Roman numeral superscripts are defined in Table 1.

Other Features of the Structure.—Table 3 compares the dimensions of the anions in the acid potassium salts of the homologous dibasic acids. The pair of central C–C bonds in KH*G* are significantly longer than the others.

The potassium ion makes contacts with two sets of four equivalent oxygen atoms. Because of the crystal symmetry, there are two independent $K^+ \cdots O$ distances and nine $O \cdots K^+ \cdots O$ angles (Table 4).

---

* For a thorough discussion of molecular vibration, relevant to the above analysis, see ref. 20.

[15] J. S. Broadley, D. W. J. Cruickshank, J. D. Morrison, J. M. Robertson, and H. H. M. Shearer, *Proc. Roy. Soc.*, 1959, *A*, **251**, 444.

[16] B. Beagley and R. W. H. Small, *Proc. Roy. Soc.*, 1963, *A*, **276**, 469.

[17] P. Coppens and T. M. Sabine, *Acta Cryst.*, 1969, **B25**, 2442.

[18] G. E. Bacon and R. J. Jude, personal communication, to be reported in *Acta Cryst.*

[19] D. W. J. Cruickshank, *Acta Cryst.*, 1956, **9**, pp. 757, 915.

[20] V. Schomaker and K. N. Trueblood, *Acta Cryst.*, 1968, **B24**, 63.

Electron-density difference syntheses carried out at the end of the least-squares refinement, with the acidic hydrogen atom omitted from F_c, showed significant density near the mid-points of all covalent bonds, as well as evidence of lone-pair electrons near each oxygen atom. The residual peak at the centre of the O · · · H · · · O bond was considerably elongated in the bond-direction, though of circular cross-section. However it shows no sign of the Kroon–Kanters–McAdam effect.[11,21,22]

EXPERIMENTAL

Preparation and Crystal Data.—KH*G* is prepared by evaporating an equimolar aqueous solution of H_2G and KOH, and is recrystallised from water, as thin plates. Normally the crystal-habit differs from that of RbH*G*; both acid salts have (100) as their most prominently developed faces, but, whereas RbH*G* is elongated parallel to b, with the forms (010) and (001), KH*G* is elongated obliquely, with (012) and (0$\bar{3}$4) developed.

TABLE 5

Comparison of crystal data

	$KH(C_5H_6O_4)$	$RbH(C_5H_6O_4)$	$NH_4H(C_5H_6O_4)$
M	170·1	216·5	149·15
a Å	18·476(4)	18·55	18·59
b Å	7·282(3)	7·57	7·56
c Å	5·133(1)	5·29	5·27
U (Å^3)	690·6	742·8	740·9
D_m	1·61	1·98	1·32
Z	4	4	4
D_c	1·636	1·935	1·33
Space group	*Cmma*	*Cmma*	*Pmaa*
μ (Mo-$K\alpha$)	7·1 cm^{-1}		

Preliminary crystal data were obtained photographically; more accurate lattice parameters were derived by a least-squares treatment of high-order reflexions whose θ values were measured on the diffractometer by use of Mo-K_α-radiation (λ = 0·71069 Å). These data are listed in Table 5, where they are compared with corresponding data for RbH*G* and NH_4HG. The diffraction symbol was $C{*}{*}a$. The more symmetrical space group *Cmma* (No. 67) was chosen because of the isomorphism with RbH*G*, and it is deemed to have been validated by the structure analysis.

Structure Determination and Refinement.—The parameters for RbH*G*[3] were the starting set. They were refined first with a limited number of photographically recorded data. Subsequently intensity data were collected on a Hilger and Watts four-circle diffractometer, using Mo-radiation with balanced filters. The crystal had the dimensions of an approximately 0·3 mm cube. The region out to θ = 35° was covered, some 900 independent reflexions being measured of which 627 were significantly above background and were used in the refinement. During the early stages of the crystal's exposure to *X*-rays, the intensities of the two standard reflexions increased, each by *ca.* 10%, and then became constant. We ascribed this initial rise to an increase of crystal mosaicity, and data collection was restarted. Absorption[23] and extinction[24] corrections were made at an appropriate, late stage of the least-squares refinement. The methylenic hydrogen atoms, which were not found in the study of RbH*G*, were located by a 'difference' electron-density synthesis, based on low-order reflexions, at the end of the isotropic stage of refinement. The final stages were by full-matrix analysis, with 14 positional parameters, 3 isotropic and 22 anisotropic vibrational parameters, and a scale-factor. There was convergence at $R = 0{\cdot}0335$ $[R' = (\Sigma w\Delta^2)/(\Sigma w|F_o|^2) = 0{\cdot}0030]$. Atomic-scattering functions were taken from ref. 25. (An extra cycle of refinement using an alternative set of functions[26] made no significant difference.) The weighting-scheme is represented by the equation, $w = [1 - \exp - \{p_1((\sin\theta)/\lambda)^2\}]/[1 + p_2|F_o|]$, where p_1 and p_2 were adjusted during the refinement, and finally took on

TABLE 6

Analysis of structure–amplitude agreement

Range	$\Sigma\|F_o\|$	$\Sigma\|F_c\|$	$\Sigma\|\Delta\|$	N *	R	$\Sigma\|\Delta\|/N$
(*a*) As a function of $\|F_o\|$						
0—3	191·99	181·96	27·25	81	0·1420	0·336
3—6	701·65	707·86	45·04	161	0·0642	0·280
6—10	1159·82	1159·36	47·53	149	0·0410	0·319
10—30	2999·82	2993·96	77·26	178	0·0260	0·434
30—50	1560·94	1563·47	36·32	40	0·0233	0·908
50—200	1384·46	1390·16	44·88	18	0·0324	2·493
(*b*) As a function of $(\sin\theta)/\lambda$						
0—0·2	879·96	896·25	35·35	16	0·0402	2·209
0·2—0·3	1387·78	1382·35	42·71	35	0·0308	1·220
0·3—0·4	1179·98	1175·21	27·37	52	0·0232	0·526
0·4—0·5	1505·86	1505·07	41·33	91	0·0274	0·454
0·5—0·6	1230·03	1232·52	38·82	122	0·0316	0·318
0·6—0·7	974·48	974·03	43·04	143	0·0442	0·301
0·7—0·8	782·95	775·22	45·47	156	0·0581	0·292
0·8—0·9	57·63	56·12	4·20	12	0·0728	0·350
All	7998·67	7996·77	278·29	627	0·0335	0·444

* N is the no. of reflexions.

---

[21] J. Kroon, J. A. Kanters, and A. F. Peerdeman, *Nature Physical Science*, 1971, **229**, 120; see also *ibid.*, **232**, 107.

[22] M. Currie and J. C. Speakman, *J. Chem. Soc.* (*A*), 1970, 1923.

[23] Program by P. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta Cryst.*, 1965, **18**, 1035, modified for KDF 9 by I. R. Mackay.

[24] Original program for KDF 9 using the method of W. H. Zachariasen, *Acta Cryst.*, 1968, **A24**, 212.

[25] 'International Tables for *X*-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1962.

[26] H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, 1964, **17**, 1040.

the respective values, 2 and 0·5. Table 6 gives a breakdown of the agreement for various sets of reflexions.

TABLE 7

Final fractional co-ordinates (× 10^5, with standard deviations in parentheses)

	x	y	z
K^+	25.000	0	0
O(1)	30.448(13)	25,000	63.508(14)
O(2)	35.859(15)	25.000	25.089(17)
C(1)	36.190(15)	25.000	48.894(18)
C(2)	43.229(15)	25.000	63.775(20)
C(3)	50.000	25.000	46.901(26)
H(0)	25.000	25.000	25.000
H(1)	50.000	14.825(355)	34.648(362)
H(2)	43.144(285)	14.736(324)	75.637(325)

Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20360 (2 pp.) 1 microfiche).* The final parameters are given in Tables 7 and 8.

TABLE 8

Vibrational parameters (10^{-4} Å^2) with standard deviations in parentheses

	U_{11}	U_{22}	U_{33}	$2U_{31}$
K^+	505(3)	403(3)	321(2)	
O(1)	198(4)	725(10)	317(5)	15(8)
O(2)	285(6)	1188(18)	322(6)	−1(10)
C(1)	210(5)	463(8)	309(6)	−11(11)
C(2)	187(5)	596(11)	341(7)	−19(10)
C(3)	189(7)	478(12)	356(11)	

	U_{iso}
H(0)	573(194)
H(1)	175(61)
H(2)	285(55)

The least-squares program for KDF 9 was that developed by Cruickshank, Smith, and Sime. We also thank Dr. Sime and others for ancillary programs, and the S.R.C. for a maintenance grant (to A. L. M.).

[2/108 *Received, January* 18*th*, 1972]

---

* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. supplied as full size copies).