Crystal Structures of Some Acid Salts of Monobasic Acids. Part XIX.[1] Potassium Hydrogen Dicrotonate, *X*-Ray and Neutron Diffraction Studies

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The crystal structure of the title compound $KH(C_4H_5O_2)_2$, has been determined, and refined to *R* 0.069 for 2199 *X*-ray, and 0.037 for 1946 neutron, reflexions. This acid salt, which is of pseudo-Type *A*, contains a hydrogen dicrotonate anion, $CH_3{\cdot}CH{:}CH{\cdot}CO_2 \cdots H \cdots O_2C{\cdot}CH{:}CH{\cdot}CH_3$, *i.e.* nearly, but not quite, symmetrical. The hydrogen bond is 'very short' [O ··· O 2.488(2), O ··· H 1.141(2), 1.348(2) Å]. This asymmetry and various minor differences between the crotonate residues are attributed to differences in O ··· K^+ contacts: in the crotonate with the shorter O ··· H, each oxygen atom makes ionic contact with a single cation, whilst in the other, each oxygen makes contact with a pair of cations. As is usual in such short OHO bonds, the relative vibrational motion of the proton appears to be a maximum along the bond direction. The geometries of the carboxy groups in this salt are compared with those of a number of Type *A* acid salts.

Ammonium and rubidium hydrogen dicrotonates are isomorphous with each other, but not with the potassium salt; and a note on these compounds is appended.

In our project on the acid salts of simple carboxylic acids, the alkali-metal salts of crotonic acid (*trans*-but-2-enoic acid, $CH_3{\cdot}CH{:}CH{\cdot}CO_2H$) have been surveyed crystallographically.[2] Only potassium hydrogen dicrotonate, $KH[C_4H_5O_2]_2$, KH[(crot)$_2$], seemed suitable for accurate study. Its i.r. spectrum (Figure 1) is of Hadži's Type (ii),[3] which implies very strong hydrogen bonding, and which led us to expect a normal Type *A*[4] structure, having the two $C_4H_5O_2$ groups of the formula crystallographically equivalent. In fact the structure is of pseudo-Type *A*: it contains hydrogen dicrotonate anions, $C_4H_5O_2HO_2{-}C_4H_5^-$, without exact symmetry. A careful study by both *X*-ray and neutron diffraction (ND) therefore seemed desirable.

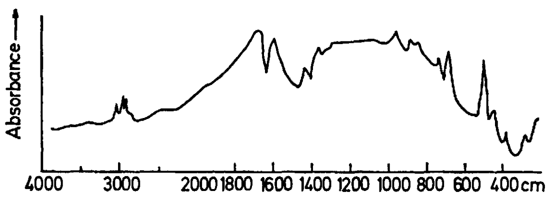

FIGURE 1 The i.r. spectrum of KH[(crot)$_2$] as a KBr disc. (By Ms. F. Lawrie, Glasgow)

EXPERIMENTAL

KH[(crot)$_2$] is easily made by dissolving crotonic acid and KOH in water (2 : 1) and allowing the solution to cool or evaporate slowly. The acid salt is very soluble in water, and a concentrated solution is necessary. Fine triclinic crystals may be formed: parallelepipeds bounded by {100}, {010} and {001}. Lattice constants, refined, by least-squares, from diffractometer angles measured by both *X*-rays (λ = 0.71069 Å = 71.069 pm) and neutrons (λ = 0.818 Å were respectively 12.453(4), 6.049(2), 7.452(2) Å, 65.62(2)° 104.04(2)°, and 97.44(2)°, and 12.465(8), 6.051(4), 7.456(6) Å, 65.61(2)°, 104.05(2)°, and 97.42(2)°.

Crystal Data.—$C_8H_{11}O_4K$, $M = 210.3$. Triclinic, $a = 12.459$, $b = 6.049$, $c = 7.452$ Å, $\alpha = 65.62°$, $\beta = 104.04°$, $\gamma = 97.44°$, $\mu = 496.0$ Å^3, $D_m = 1.37$, $Z = 2$, $D_c = 1.408$, $\mu(\text{Mo-}K_\alpha) = 5.1$ cm^{-1}. Space group $P\bar{1}$ (No. 2): justified by the outcome of the analysis. Operation with the matrix 010/0—11/100 leads to the Dirichelet-reduced cell with parameters 6.049, 7.410, 12.459 Å, 98.0°, 97.4°, and 113.7°.

X-Ray Analysis.—The structure was solved by the heavy-atom method from limited photographic-visual intensity data.[2] Subsequently X-ray intensities were measured on a Hilger and Watts four-circle diffractometer, with graphite-monochromated Mo-K_α radiation. A crystal, with dimensions (mm) 0.6 × 0.4 × 0.25, was mounted near to *c* and parallel to its greatest length. Intensities were collected in two shells: set *I*, 1 734 independent reflexions out to θ 25°, reduced to 1 614 by the criterion $I > 2\sigma(I)$; set *II*, some 850 out to 29°, reduced to 585. Standard deviations (σ) were estimated from counting statistics, and structure amplitudes were weighted accordingly. In the later stages of full-matrix least-squares refinement (with the CRYLSQ program of the '*X*-Ray '72' System),[5a] the sets were combined; and in the final cycles 75 terms with sin θ < 0.15 were omitted as they seemed to suffer from extinction and other small errors.† Scattering factors were taken from ref. 5(*b*) those for K^+ being corrected for dispersion. The vibrations of the H atoms were assumed isotropic, those for other atoms anisotropic. The final *R*(*F*) value was 0.069, whilst *S*, the standard deviation of an observation of unit weight, was 3.3. Apart from some minor overweighting of terms with low θ, analysis showed the weighting scheme to be satisfactory. Final co-ordinates are listed in Table 1, the upper values referring to the *X*-ray results. The numbering of atoms is explained in Figure 2. Symmetry-related units needed in the description of the structure are coded thus: CCU x, y, z; i, $x, -1 + y, z$; ii, $1 - x, 1 - y, 2 - z$; iii, $1 - x, 2 - y, 1 - z$; and iv, $x, 1 + y, z$.

Neutron Diffraction Analysis.—A crystal of volume *ca.* 10 mm^3 was used: normal distances between opposite {100}, {010} and {001} faces were 0.9, 2.5, and 3.9 mm respectively. It was mounted with *c* near the principal axis

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† Naturally, excision of these terms improved *R*; but it justified itself by also improving the standard deviations a little. The 75 terms omitted have been included as an appendix to the deposited *X*-ray structure-factor table.

[1] Part XVIII, G. E. Bacon, C. R. Walker, and J. C. Speakman, *J.C.S. Perkin II*, 1977, 979.

[2] D. R. McGregor, Ph.D. Thesis, University of Glasgow, 1967.

[3] (*a*) D. Hadži, *Pure Appl. Chem.*, 1965, **11**, 435; (*b*) D. Hadži and S. Bratos, in 'The Hydrogen Bond,' eds. P. Schuster, G. Zundel, and C. Sandorfy, vol. II, North Holland, Amsterdam, 1976, ch. 12; (*c*) A. Novak, *Structure and Bonding*, 1974, **18**, 177.

[4] J. C. Speakman, *Structure and Bonding*, 1972, **12**, 141; M. Currie and J. C. Speakman, *J. Chem. Soc.* (*A*), 1970, 1923.

[5] (*a*) '*X*-Ray' program system, University of Maryland, Technical Report TR 192, 1972; (*b*) 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962; (*c*) M. S. Lehmann and F. K. Larsen, *Acta Cryst.*, 1974, **A30**, 580.

of the goniometer-head. Intensities were measured, with neutrons of wavelength 0.818 Å, on the diffractometer D9 at the Institut v. Laue-Langevin High Beam-Flux Reactor, Grenoble. Scanning was by ω-steps, the range for each reflexion being chosen, as a function of 2θ, so as to equalise times spent on peak and background.[5c] A hemisphere of reciprocal space, explored to (sin θ)/λ = 0.7 Å^{-1}, yielded 2 876 independent reflexions which were reduced to 1 946 by the condition $F_o{}^2 > 3\sigma(F_o{}^2)$, σ being the standard deviation based on counting statistics. Absorption corrections were applied, using a Gaussian integration.[6] The coefficient had been measured directly and found to be 1.49 (2) cm^{-1}, which implies an incoherent scattering cross-section for H of 33 barns as the principal source of absorption.

TABLE 1

Fractional co-ordinates (× 10^5), with standard deviations in parentheses. *X*-Ray results are given above those for ND below

	x	*y*	*z*
K	409 80(5)	461 25(10)	714 46(10)
	409 67(17)	461 50(32)	714 38(33)
O(1)	237 98(19)	707 05(39)	706 63(39)
	237 93(11)	706 85(23)	706 79(24)
O(2)	319 99(17)	995 27(36)	810 42(38)
	320 13(10)	994 26(23)	810 78(23)
O(3)	500 11(16)	826 17(32)	847 72(31)
	499 99(9)	826 53(19)	847 30(20)
O(4)	548 02(18)	120 241(34)	654 56(33)
	547 88(11)	120 258(20)	654 60(21)
C(1)	233 55(22)	880 76(47)	748 43(41)
	233 56(8)	880 84(17)	748 13(16)
C(2)	124 72(25)	972 51(56)	728 82(50)
	124 55(9)	971 62(20)	728 10(19)
C(3)	110 60(27)	115 403(59)	773 16(53)
	110 50(10)	115 387(22)	773 52(20)
C(4)	158(34)	124 702(71)	754 47(64)
	140(14)	124 749(30)	754 83(29)
C(5)	565 09(22)	981 05(44)	744 21(38)
	565 03(8)	982 83(16)	743 83(15)
C(6)	665 87(24)	892 16(51)	728 28(47)
	666 29(9)	893 02(18)	727 50(18)
C(7)	693 85(24)	663 88(50)	805 86(45)
	693 42(9)	662 62(19)	805 96(18)
C(8)	793 47(32)	572 92(74)	783 68(63)
	793 10(12)	572 37(28)	783 04(25)
H(0)	388 74(536)	919 35(1 125)	819 83(988)
	402 07(20)	917 50(39)	824 48(40)
H(2)	5 478(961)	870 63(2 041)	671 72(1 825)
	5 403(25)	873 83(70)	675 58(71)
H(3)	17 653(389)	124 808(805)	80 261(675)
	18 196(27)	124 119(63)	82 866(68)
H(6)	70 696(425)	101 248(838)	64 549(751)
	71 820(26)	103 126(48)	63 927(59)
H(7)	54 033(496)	50 963(1 020)	89 296(882)
	64 100(24)	52 764(46)	89 495(54)
H(41)	−4 906(601)	116 530(1 208)	71 379(1 066)
	−6 587(37)	117 529(131)	68 213(122)
H(42)	−311(893)	149 934(1 839)	66 915(1 740)
	64(42)	143 455(79)	67 822(87)
H(43)	−1 588(472)	122 287(1 004)	87 875(838)
	−1 327(37)	122 319(95)	89 219(75)
H(81)	76 334(631)	44 070(1 226)	73 438(1 102)
	77 272(38)	42 925(100)	73 761(99)
H(82)	81 778(397)	72 970(833)	67 407(737)
	83 562(37)	70 763(79)	68 175(76)
H(83)	84 030(490)	54 429(1 011)	90 289(849)
	84 913(32)	49 594(85)	92 198(69)

The early stages of full-matrix, anisotropic least-squares refinement were done at Glasgow with CRYLSQ, final cycles at Grenoble with LINEX74,[6] which minimises $\Sigma w|F_o{}^2 - kF_c{}^2|^2$; $w = \{(\sigma^2 + 0.02F_o{}^2)^2\}^{-1}$. Extinction was treated anisotropically in the type $\bar{I}$ Lorentzian approximation;[7] the correction factors were < 1.1 for nearly all reflexions, though a few terms needed larger factors, the greatest being 2.1 for the 100 reflexion. Scattering amplitudes were (K) 0.37, (O) 0.58, (C) 0.665 and (H) −0.374 × 10^{-12} cm. At convergence $R(F)$ was 0.040, $R(\omega F)$ 0.037 and $R(F^2)$ 0.052; $S = 1.95$. Analysis showed the weighting-scheme to be satisfactory, apart from a small tendency to overweight high-angle reflexions. Final ND structure factors have been deposited along with those from the *X*-ray study and the thermal parameters from the latter, in Supplementary Publication No. SUP 22043 (15 pp., 1 microfiche).* Thermal parameters from the ND study are appended as Table 1a.

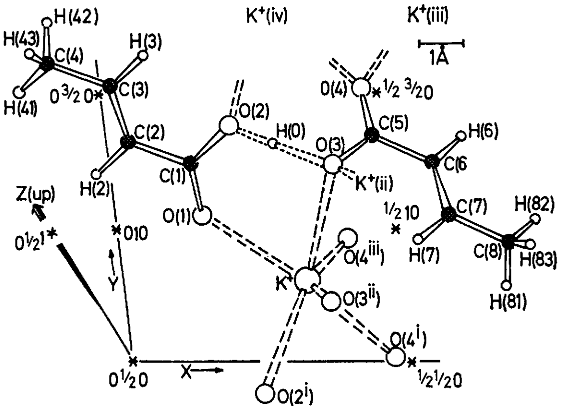

FIGURE 2 The structure seen in projection down the *c′* axis of an orthogonal set. The hydrogen bond is shown by dotted lines, ionic contacts by broken lines. Some, but not all, centres of inversion are marked by asterisks

RESULTS AND DISCUSSION

Without prior knowledge of the structure of KH[(crot)$_2$], apart from the fact that it was an acid salt of crotonic acid, Dr. Lindgren (Uppsala), in collaboration with Professor Grenthe (Stockholm), examined the spectrum (see Figure 1†). They then wrote [8b] 'If one of the peaks at 1673/1652 cm^{-1} is due to the C–O stretch, then the hydrogen bond is asymmetric with OH · · · O 2.48 A; this is a compound of pseudo-Type *A*'. Professor Hadži (Ljubljana) also, and independently, deduced from the spectrum that the system was 'certainly asymmetric.'[8b] The remarkable accuracy of these predictions is borne out by the results we now present, and is illustrated in the stereoscopic view in Figure 3 as well as in Figure 2.

We shall refer to the two non-equivalent crotonate residues as (*M*) [C(1)—(4), O(1), O(2)] and (*J*) [C(5)—(8), O(3), O(4)]. Interatomic distances and angles within and between (*M*) and (*J*) are listed in Table 2. Apart

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1975, Index issue.

† The spectrum produced in Uppsala had better resolution than that shown in Figure 1.

[6] Programs DATAPH and LINEX74, P. Coppens, personal communication from the Buffalo Crystallographic Computing System.

[7] P. J. Becker and P. Coppens, *Acta Cryst.*, 1974, **A30**, 129; 1975, **A31**, 417.

[8] (*a*) Personal communication from I. Grenthe; see also R. Svanfeldt, J. Lindgren, and I. Grenthe, *Acta Chem. Scand.*, 1975, **A28**, 1129; (*b*) personal communication.

from details involving H atoms, the agreement between X-ray and ND results is excellent. In discussing the structure we shall normally cite the latter, as they are more precise. The only difference, between the heavy-atom structures, of probable significance is that the C–C distances found by X-rays are slightly smaller, and the C–C–C angles slightly greater. This may be attributed to the asphericity errors in X-ray work, whereby, for instance, carbon atoms are shifted towards the centre of a benzenoid ring.[9]

TABLE 1a

Vibrational parameters ($Å^2$, × 10^4) from the ND analysis

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
K	487(11)	282(8)	548(12)	59(7)	198(9)	−162(8)
O(1)	425(6)	397(6)	694(10)	31(5)	158(6)	−288(6)
O(2)	345(6)	381(6)	720(9)	22(5)	172(6)	−290(6)
O(3)	326(5)	282(5)	508(7)	44(4)	157(5)	−116(5)
O(4)	467(6)	264(5)	527(8)	102(5)	197(6)	−78(5)
C(1)	320(5)	292(4)	437(6)	45(4)	143(4)	−122(4)
C(2)	338(5)	449(6)	558(7)	96(5)	118(5)	−200(5)
C(3)	436(6)	423(6)	592(8)	108(5)	207(6)	−164(5)
C(4)	564(9)	638(9)	751(11)	271(7)	272(8)	−148(8)
C(5)	301(4)	258(4)	371(5)	63(3)	93(4)	−108(4)
C(6)	370(5)	331(5)	512(7)	96(4)	192(5)	−82(5)
C(7)	366(5)	364(5)	483(7)	133(4)	120(5)	−120(5)
C(8)	510(7)	587(8)	655(9)	265(7)	208(7)	−144(7)
H(0)	583(13)	433(1)	686(15)	−2(9)	179(11)	−251(11)
H(2)	470(15)	1 136(26)	1 701(38)	81(16)	54(19)	−1 006(27)
H(3)	616(19)	948(22)	1 701(39)	−11(16)	338(21)	−910(26)
H(6)	782(18)	515(14)	1 367(30)	127(13)	713(21)	37(16)
H(7)	694(16)	467(13)	1 148(25)	116(12)	447(17)	−71(15)
H(41)	520(21)	2 451(70)	2 927(85)	466(30)	−89(32)	−1 960(68)
N(42)	1 334(36)	882(27)	1 728(45)	541(26)	718(34)	−90(28)
H(43)	1 148(32)	1 576(39)	1 157(34)	641(29)	571(27)	−290(29)
H(81)	1 012(31)	1 513(41)	2 305(62)	363(28)	339(35)	−1 395(42)
H(82)	1 187(30)	1 104(29)	1 536(39)	501(24)	997(31)	163(27)
H(83)	778(22)	1 486(36)	1 052(29)	695(25)	145(21)	−159(27)

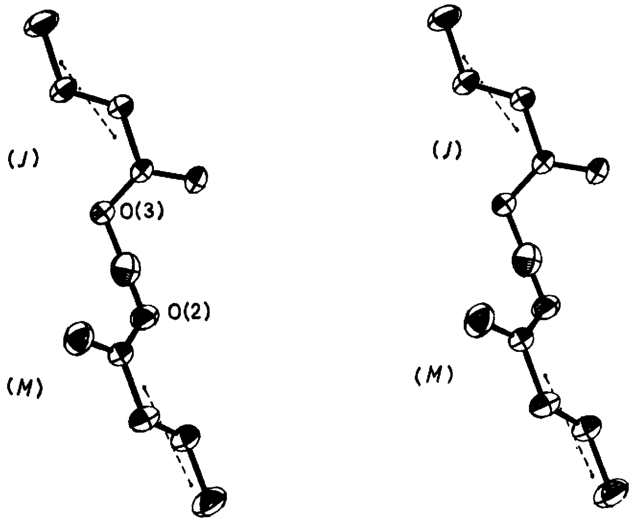

FIGURE 3 Stereoscopic views of the hydrogen dicrotonate anion, $(CH_3{\cdot}CH{=}CH{\cdot}CO_2 \cdots H \cdots O_2C{\cdot}CH{=}CH{\cdot}CH_3)^-$. Broken lines indicate the directions of the axes of maximum rigid-body libration of the two independent crotonate residues. For clarity, only the acidic proton, H(0), is shown. (Produced from the ND results by C. K. Johnson's ORTEP program)

The Hydrogen Bond.—Table **3** collects information[1,10–19] on some dozen Type *A* salts of carboxylic acids which contain symmetrical, or 'symmetry-related',[20] OHO bonds, and which have been studied with fair precision. (We have omitted cases where the hydrogen bonding is intramolecular and where compressional stress is probable.) The average O $\cdots$ O distance is 2.449 Å. In contrast the bond in $KH[(crot)_2]$ is significantly longer [2.4879(15) Å], and the proton is 0.1 Å off-centre. It still shows the inverted vibrational behaviour characteristic of 'very short' OHO bonds;[1,21] the mean-square amplitudes of the proton relative to the neighbouring oxygen atoms, are $U_{(\parallel)}$ 0.027, $U_{(\perp)}$ 0.010 and 0.006 $Å^2$ respectively, the first corresponding to a root-mean-square amplitude of 0.17 Å. We have looked for a KKM effect[13,16,22] by way of an $(X—N')$ synthesis, using all the X-ray data of set *I*: N' is the X-ray structure factor calculated from the ND parameters, for all atoms except

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[9] See *e.g.* P. Coppens, 'International Review of Science, Physical Chemistry, Ser. 2, vol. 11, 'Chemical Crystallography,' ed. J. M. Robertson, Butterworth, 1975, ch. 2.

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TABLE 2

Geometrical details in, and between, crotonate residues. [distance (Å), angles (°), standard deviations in parentheses]

		X-Ray	ND	ND (corr.)
(M)	C(1)–O(1)	1.224(3)	1.223 3(16)	1.233
	C(1)–O(2)	1.297(4)	1.296 3(17)	1.315
	C(1)–C(2)	1.483(4)	1.481 7(14)	1.488
	C(2)–C(3)	1.313(4)	1.321 9(16)	1.332
	C(3)–C(4)	1.491(5)	1.493 4(16)	1.500
	C(2)–H(2)	1.10(12)	1.079(4)	
	C(3)–H(3)	0.97(5)	1.059(4)	
	C(4)–H(41)	0.83(7)	1.033(7)	
	C(4)–H(42)	1.39(10)	1.036(5)	
	C(4)–H(43)	0.95(5)	1.031(5)	
	O(2)–H(O)	1.00(6)	1.140 7(25)	
(J)	C(5)–O(3)	1.280(3)	1.283 8(15)	1.300
	C(5)–O(4)	1.245(3)	1.236 8(14)	1.245
	C(5)–C(6)	1.476(4)	1.486 0(13)	1.491
	C(6)–C(7)	1.315(4)	1.323 6(14)	1.330
	C(7)–C(8)	1.491(5)	1.491 7(17)	1.496
	C(6)–H(6)	0.93(5)	1.078(3)	
	C(7)–H(7)	1.13(6)	1.076(3)	
	C(8)–H(81)	1.01(7)	1.035(6)	
	C(8)–H(82)	1.03(5)	1.045(5)	
	C(8)–H(83)	0.90(6)	1.054(5)	
	O(3)–H(0)	1.50(6)	1.347 6(24)	
	O(2) · · · O(3)	2.493(3)	2.487 9(15)	
(M)	O(1)–C(1)–O(2)	123.9(3)	123.64(11)	124.2
	C(2)–C(1)–O(1)	120.1(3)	119.75(10)	119.2
	C(2)–C(1)–O(2)	116.1(2)	116.51(10)	116.6
	C(1)–C(2)–C(3)	125.0(3)	124.62(10)	124.0
	C(2)–C(3)–C(4)	125.4(3)	125.40(12)	124.7
(J)	O(3)–C(5)–O(4)	123.9(2)	124.15(11)	124.6
	C(6)–C(5)–O(3)	118.2(2)	117.83(9)	117.9
	C(6)–C(5)–O(4)	117.9(2)	118.02(9)	117.5
	C(5)–C(6)–C(7)	125.7(3)	125.20(10)	124.7
	C(6)–C(7)–C(8)	125.8(3)	125.03(11)	124.5
	O(2) · · · H(0) · · · O(3)	172.5(6)	177.99(26)	
	C(1)–O(2) · · · H(0)	110(3)	114.0(2)	
	C(5)–O(3) · · · H(0)	115(2)	113.2(1)	
Dihedral angles				
	O(2)–C(1)–C(2)–C(3)		−1.5(2)	
	O(3)–C(5)–C(6)–C(7)		2.3(2)	

TABLE 3

Comparison of the geometries of carboxy-groups engaged in Type A hydrogen bonding [distances (Å), angles(°)]

	Symm.	Method	O · · · O	Σr	Δr	$\Delta\theta$
KH bis(phenylacetate) [a]	$\bar{1}$	X	2.451(4)	2.507	0.067	−6.7
		ND	2.454(3)	2.512	0.062	−6.5
NaH diacetate * [b]	2	ND	2.453(2)	2.533	0.062	−5.3
KH diaspirinate	$\bar{1}$	X [c]	2.456(4)	2.505	0.063	−6.9
		ND [d]	2.448(4)	2.501	0.067	−6.7
$KH(F_3C{\cdot}CO_2)_2$ [e]	$\bar{1}$	ND	2.437(4)	2.480	0.052	−8.3
$KD(F_3C{\cdot}CO_2)_2$ [e]		ND	2.437(3)	2.486	0.056	−8.4
KH malonate [f]	$\bar{1}$	X	2.459(5)	2.516	0.070	−11.9
KH glutarate [g]	$\bar{1}$	X	2.445(3)	2.522	0.076	−9.0
KH *meso*-tartrate * (Type A bond) [h]	$\bar{1}$	X	2.452(2)	2.526	0.068	−9.4
KH acetylenedicarboxylate [i]	$\bar{1}$	X	2.445(3)	2.505	0.063	−5.7
KH succinate [j]	2	X	2.446(4)	2.526	0.076	−9.3
RbH oxydiacetate [k]	2	ND	2.449(3)	2.508	0.070	−9.8
Means			2.449(2)	2.510(4)	0.066(2)	−8.0(5)
KH(crot)$_2$	Residue (M)	X	2.493(3) 2.487 9(15)	2.531	0.073	−4.1
		ND		2.520	0.073	−3.3
	Residue (J)	X		2.535	0.043	0.5
		ND		2.520	0.047	−0.2

* At low temperature.

[a] Ref. 1. [b] Ref. 10. [c] Ref. 11. [d] Ref. 12. [e] Ref. 13. [f] Ref. 14. [g] Ref. 15. [h] Ref. 16. [i] Ref. 17. [j] Ref. 18. [k] Ref. 19.

H(O). There was no sign of the characteristic double peak, though our X-ray intensities were not accurate enough to give a clean background. The simplest model to accommodate our results is that of a proton moving in a shallow, and effectively single-minimum, potential well which is markedly skew because the environment is unsymmetrical. That the comparatively slight differences between residues (M) and (J) are sufficient to cause a large shift in the point of minimum energy is further evidence for a shallow potential.

The Double Anion.—As the details in Table 2 show, residues (M) and (J) are structurally similar. Indeed, for the most part, they are ' chemically ' identical, but the OHO bond is very unsymmetrical, and we must look for small differences which may answer the question why KH[(crot)$_2$], having got so near, does not crystallise in a Type A pattern. Each crotonate anion has its atoms, except methylic H, nearly coplanar. The mean planes through the six heavier atoms are represented by the equations:

$$(M)\ -0.17838\,X' - 0.27357\,Y' + 0.94157\,Z' = 2.50934\ \text{Å}$$

$$(J)\ \ 0.29621\,X' + 0.49198\,Y' + 0.81867\,Z' = 9.44183\ \text{Å}$$

where X', Y', and Z' are absolute, orthogonal co-ordinates; M is more nearly planar, the largest deviation being 0.013 Å and χ^2 190 for three degrees of freedom. The largest deviation from the (J) plane is 0.034 Å, with χ^2 1 327. If this were a Type A structure, the two mean planes would be exactly parallel. The angle between the two planes is actually 54°, or from another aspect, the dihedral angle C(1)–O(2) · · · O(3)–C(5) is 123°.

Molecular-vibration analysis, by the method of Schomaker and Trueblood,[23] was applied to the ND parameters. Each set of six C or O atoms fitted the rigid-body model very well, the root-mean-square ΔU_{ij} being 0.0010 for (M) and 0.0008 Å^2 for (J). Translational vibration of the bodies was roughly isotropic; libration was decidedly maximal about axes near to those of minimum moment of inertia. These axes are marked

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

with broken lines in Figure 3. The root-mean-square amplitudes of libration, about principal axes of increasing inertia are 9.5, 3.6, and 1.7° for (*M*), and 8.7, 3.1, and 1.8° for (*J*). Interatomic distances corrected for such libration, where appropriate, are in column 4 of Table 2. There are obvious signs of high-amplitude internal oscillation of the methyl groups. Their root-mean-square amplitudes, in excess of the rigid-body motion, were estimated to be 23° in (*M*) and 20° in (*J*). Allowance for the consequent shrinkage errors raises the average C-H distances from 1.033 (*M*) and 1.045 Å (*J*) to 1.119 and 1.120 Å.

Apart from their orientations, the only differences between (*M*) and (*J*) lie in their carboxy-groups. Table 3 compares some geometrical quantities for these non-equivalent groups with those for the $-CO_2HO_2C-$ units in Type *A* structures, where the carboxy-groups are space-group equivalent. The results for the latter constitute a uniform set. Averages are given for the various dimensions, with their statistical standard deviations, which, of course, are significant only as rough measures of scatter. The difference between the C-C-O angles $\Delta\theta$, is more variable than the C-O difference, Δr. [Paul[24] has published a correlation graph between these two differences in a series of centrosymmetric carboxylic acid dimers. Though the context appears incongruous, it is interesting to find that the averages in Table 3 (0.06 Å and −8.0) yield a point not far from Paul's correlation line.]

For KH[(crot)$_2$] Δr and $\Delta\theta$ are qualitatively in the sense that would be required if (*M*) corresponded to RCO_2H and (*J*) to RCO_2^-. Quantitatively they are anomalous. The differences for (*J*) would not arouse undue surprise, were the carboxy-group fully ionised; but for (*M*) the differences are too small for an un-ionised group that is free from disorder, and $\Delta\theta$ is even too small for the 'half-ionised' group in a Type *A* structure.

Otherwise the crotonate residues are almost identical geometrically. A possible exception is the difference (0.004 Å) between C(1)—C(2) and C(5)—C(6). The near-equality of C-O distances and C-C-O angles in (*J*) suggests better conjugation within this carboxy-group; hence there may be rather less cross-conjugation between it and the neighbouring double bond than in (*M*). In both residues the C-C bonds involving the methyl groups are larger (4σ) than the inner C-C bonds; the former involve one carbon atom that is sp^3-hybridised whereas both carbons of the latter are sp^2-hybridised.

$K^+\cdots O$ *Interactions*. Consideration of the internal geometry of the double-anion leaves us without explanation of its asymmetry, and with additional anomalies. We turn now to its external contacts. The potassium ion makes six $K^+\cdots O$ contacts, details of which are listed in Table 4. We have used the *X*-ray results here, though they agree with those from ND, because they are marginally more precise in their location of the cation. The majority of the acid potassium salts in Table 3 have the potassium ion co-ordinated to eight, or more, oxygen (or other negative) atoms, and mean $K^+\cdots O$ 2.87 Å. In the phenylacetate, aspirinate, and acetylenedicarboxylate, there is six-co-ordination; the mean interatomic distance is then smaller (2.79 Å) and the cation must produce a stronger electrostatic field at the oxygen atoms.

TABLE 4

Geometry of the potassium-ion environment [distances (Å), angles (°), *X*-ray results only]

$K^+\cdots O(4^{i})$	2.693 3(20)	$K^+\cdots O(3)$	2.783 7(20)
$K^+\cdots O(1)$	2.736 6(21)	$K^+\cdots O(4^{iii})$	2.789 6(22)
$K^+\cdots O(2^{i})$	2.579 7(21)	$K^+\cdots O(3^{ii})$	2.995 5(21)
Angles at K^+:			
$O(4^{i})\cdots O(1)$	167.38(7)	$O(2^{i})\cdots O(3)$	147.37(7)
$O(4^{i})\cdots O(2^{i})$	72.75(6)	$O(2^{i})\cdots O(4^{iii})$	128.95(7)
$O(4^{i})\cdots O(3)$	118.39(6)	$O(2^{i})\cdots O(3^{ii})$	72.27(6)
$O(4^{i})\cdots O(4^{iii})$	80.76(6)		
$O(4^{i})\cdots O(3^{ii})$	84.43(6)	$O(3)\cdots O(4^{iii})$	83.66(6)
$O(1)\cdots O(2^{i})$	101.77(7)	$O(3)\cdots O(3^{ii})$	78.26(6)
$O(1)\cdots O(3)$	72.44(6)		
$O(1)\cdots O(4^{iii})$	94.77(7)	$O(4^{iii})\cdots O(3^{ii})$	147.53(6)
$O(1)\cdots O(3^{ii})$	105.00(7)		

Additional distances: $O(1)\cdots H(0)$ 2.440(3), $O(4)\cdots H(0)$ 2.526(3)

In KH[(crot)$_2$] there is also six-co-ordination. The ionic bonding is strong, with mean $K^+\cdots O$ 2.79 Å. Further, it is unevenly applied to the double anion. The oxygen atoms of (*M*) make only one contact each with K^+; those of (*J*) each make a pair of contacts. To O(4) the contacts are exceptionally strong, mean 2.74 Å; they are mutually inclined at 81°, and their bisector is not far from the line of C(5)-O(4) extended. Round O(3) one K^+ is at 3.00 Å, but there is also the short contact to H(0); in all there are four bonds, to C(5), H(0), K^+, and K^+ (ii), in directions corresponding to a not-very-irregular tetrahedron. That their ionic environment weakens all the C-O bonds, and those in (*J*) particularly, offers a satisfactory explanation of the anomalies described above.

The firmer bonding of O(3) and O(4) also explains the less vigorous libration of residue (*J*) in comparison with (*M*).

With the idea of quantifying the competition in KH[(crot)$_2$] between hydrogen bonding and ionic contacts to K^+, we have applied the bond-valence concept of Brown and Shannon.[25a] Distances from oxygen to H(0) were converted into bond valences (*s*) graphically;[25b] those to K^+ and carbon by the equations,[25c] $s = \{r(K^+\cdots O)/2.279\}^{-9.1}$ and $s = \{r(C-O)/1.378\}^{-4.065}$. Results, in *v.u.*, are set out in Table 5. The balance is satisfactory; whilst the drainage of valence to *K*$^+$ from the carboxy-group of (*J*), which is greater than that from (*M*) by 0.25 *v.u.*, accords with a hydrogen-bond valence reduced by 0.18. For comparison we have applied the same treatment to the half-unit of potassium hydrogen bis(phenylacetate), a centro-symmetric, Type *A* acid salt.[1] These results are also appended to Table 5. Though the

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[24] See *e.g.* D. A. Dieterich, I. C. Paul, and D. Y. Curtin, *J. Amer. Chem. Soc.*, 1974, **90**, 6378.

[25] (*a*) I. D. Brown and R. A. Shannon, *Acta Cryst.*, 1973, **A29**, 266; (*b*) I. D. Brown, *ibid.*, 1976, **A32**, 24; (*c*) I. D. Brown and K. K. Wu, *ibid.*, 1976, **B32**, 1957.

extension of Brown's methods to carboxylates implies an extrapolation beyond the types of crystal for which they were developed, the outcome is plausible.

The hydrogen bond is significantly bent: the proton H(0) lies 0.022 Å off the O(2) · · · O(3) line, and roughly in the direction from K^+(iv) towards K^+. The distances $K^+ \cdots$ H(0) and H(0) $\cdots K^+$(iv) being respectively 3.204 and 3.040(3) Å, the shift is attributable to cation repulsion. At such distances, the effect of the potassium ions on the proton must be electrostatic, and not of ordinary van der Waals character. A simple calculation shows that the displacement of the proton by a pair of opposite univalent cations at r_1 and r_2 (Å) would be $(23.1 \times 10^{-4}/f)(1/r_1^2 - 1/r_2^2)$, where f is a force constant opposing motion of the proton across the hydrogen bond. Adopting 10^5 dyne cm^{-1} as of the correct order for f, we find a displacement of 0.025 Å. The agreement is fortuitous, but it suggests that displacement of the amount observed can reasonably be explained in this way.

TABLE 5

A bond-valence analysis (see text)

	K^+	H(0)	C(1) or C(5)	Σ (at O)	
O(1)	0.19	0.06	1.62	1.87	
					(*M*)
O(2)	0.17	0.53	1.28	1.98	
	0.36	0.59	2.90	3.85	
O(3)	0.16 0.08	0.37	1.33	1.94	
					(*J*)
O(4)	0.21 0.16	0.04	1.55	1.96	
	0.61	0.41	2.88	3.90	
	0.97	(1.00)	5.78	7.75	

Potassium hydrogen bis(phenylacetate)

	K^+	H(1)	C(1)	Σ (at O)
O(1)	0.15 0.12	0.05	1.61	1.93
O(2)	0.21	0.45	1.32	1.98
	0.48	(0.50)	2.93	3.91

This idea may have wider applications. In Type *A* systems where there is a centre of symmetry involved, the proton is, formally, required to be exactly at the midpoint between the oxygen atoms. Where the symmetry arises from a two-fold axis (or a mirror-plane), this is not necessary. In the examples given in Table 3 where the symmetry is 2, ND shows a significant displacement of the proton from the mid-point. These amount to 0.055(3) and 0.053(4) Å in refs. 10 and 19, and 0.107 Å in ref. 18. In every case the direction of the displacement, along the two-fold axis, is away from cations which are relatively close, and towards a region which is electrostatically neutral. A recent example is $CsH[NO_3]_2$, whose crystal contains a strong OHO bond across a two-fold axis.[26] On either side of this bond, along the axis, are Cs^+ at 5.6 and 7.4 Å. The proton is shifted away from the former by 0.079 Å.

One of us has suggested that the exact symmetry obtaining in Type *A* crystals may help to stabilise and shorten the OHO bonds.[4] Exception has been taken to this view: ' the data do not support this otherwise reasonable suggestion '.[27] The point is appreciated. But the present results show, at least, that, where there is no site-symmetry, the way becomes open to unilateral effects which must of course, render the OHO bond unsymmetrical, and may also weaken it.

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APPENDIX

Acid ammonium rubidium salts of crotonic acid were prepared in the expectation that they would be isomorphous with KH[(crot)]$_2$] and so assist in the solution of the phase problem. They proved to be isomorphous with one another, but not with the potassium salt. Crystallographic measurements on rubidium hydrogen dicrotonate, which consisted of soft, hygroscopic crystals, were as follows: $C_8H_{11}O_4Rb$, $M = 256.5$, Orthorhombic, $a = 33.1$, $b = 17.46$, $c = 7.62$ Å, $\mu_c = 4\,404$ Å^3, $D_m = 1.52$, $Z = 16$, $D_c = 1.55$. Space group $P2_12_12$ (No. 18). (If some weak reflexions were ignored, *Pccn*). With 52 (non-hydrogen) atoms in the asymmetric unit, this was not a promising material for accurate structure analysis; it was made worse by the rapid fall-off of intensity with θ, and by the probable presence of disorder. However, an approximate structure was determined, and a set of 1 269 structure factors is given in ref. 2. At least some of the crotonate residues appear to occur as asymmetric double anions like those in KH[(crot$_2$)].

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[26] J. Roziere, M.-T. Roziere-Bories, and J. M. Williams, *Inorg. Chem.*, 1976, **15**, 2490.

[27] J.-O. Lundgren and I. Olovsson, ref. 3(*b*), ch. 10.